VOL. XI. 1907

TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY.

C. F. Burgess

TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

VOLUME XI.

ELEVENTH GENERAL MEETING

PHILADELPHIA, MAY 2, 3 AND 4, 1907.

PUBLISHED BY
THE AMERICAN ELECTROCHEMICAL SOCIETY
LEHIGH UNIVERSITY, SOUTH BETHLEHEM, PA.
1907

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APPENDIX.

ERRATA.

Pages 122, 124, 126, 128, 130, 132, *head lines,* for Snowden read Snowdon.

VOLUME XI. 1907.

TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

PROCEEDINGS

CONDENSED MINUTES OF THE ELEVENTH GENERAL MEETING OF THE SOCIETY, HELD AT THE UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA,
MAY 2, 3 AND 4, 1907.

Number of members registered, 123; guests, 8; total, 131.

SESSION OF MAY 2nd.

The meeting was called to order at 10 A. M., in the lecture room of the John Harrison Chemical Laboratory, by President Carl Hering, who greeted the Society as follows:

"LADIES AND GENTLEMEN: I take pleasure in opening the Eleventh General Meeting of the American Electrochemical Society. Those of you who have been members of this Society from the beginning will remember that our inaugural meeting was held in this very hall. The first item on the program is an address of welcome by Dr. Edgar F. Smith, Professor of Chemistry at this University, also its Vice-Provost, and, furthermore, a renowned electrochemist and member of our Society."

VICE-PROVOST EDGAR F. SMITH: "MR. PRESIDENT AND FELLOW-MEMBERS OF THE AMERICAN ELECTROCHEMICAL SOCIETY: On behalf of the Provost of the University and the Trustees, I extend to you the most cordial welcome. We have great pleasure in having you meet here. It is a matter of great interest to us that this Society at its formation saw fit to hold its first meeting at the University of Pennsylvania. Those who are familiar with the history of chemical teaching in America know that the first chemical society in America was founded in Philadelphia, and by those who were engaged in the teaching of chemistry in our University. This was in 1792. In 1812 the second chemical society in this country was founded here in Philadelphia, and was conducted by professors and students of our University; at the founding of the American Chemical Society, in 1874, at the grave of the great Joseph Priestley, it was the professor of chemistry in this University who made the suggestion that a national chemical society be formed; so that the University has always had profound interest in things chemical.

Hence, it is a matter of no little moment that this, the youngest of the chemical societies, or of societies taking into consideration affairs chemical, should have held its first meeting in the University, and now its eleventh meeting. I would like to recall, too, the fact that while this is the American Electrochemical Society, one of our early professors of chemistry—the great Robert Hare, who assumed the duties of the chair in the year 1818—did much that would have been of interest to us. Had there been an American Electrochemical Society in that day, he no doubt would have been a most active member. It is to him we owe the compound blowpipe; it is to him that we are indebted for the calcium light—the Drummond light. It was in 1820 that Hare devised the so-called calorimoter, by which he obtained electricity of great intensity. Four years prior to that he devised the deflagrator, with which instrument Benjamin Silliman, the elder, was able to melt and volatilize carbon, as he said. The deflagrator was the forerunner of the Bunsen battery. As we read the researches of Michael Faraday and observe how he sought for something superior to the old Voltaic pile, he finally admits that the deflagrator of Robert Hare was the thing needed for his work; he used it, and acknowledges his great indebtedness to him for that discovery.

Again, in 1838, Robert Hare, after carefully scrutinizing the work of Humphrey Davy on the isolation of the alkaline earthy metals, set his deflagrator to work upon a solution of calcium chloride, using mercury as the cathode, obtaining an amalgam, which he afterwards distilled and got the metal calcium, of a silver-gray color, of a specific gravity nearly equal to that of the calcium which has recently been isolated, and able to give its properties more correctly than had ever been given before. I repeat, the University, therefore, has interest in the meeting of this Society, because of the work of many of its earlier professors, particularly the work of Robert Hare; and in recent times, too, we have followed, after a fashion, in the footsteps of that great master, and have tried to do, in our humble way, a little investigation along these lines—not especially the lines that the engineer follows, but the lines that a chemist would follow using electricity as his reagent.

But I am not here to occupy much of your time; I have come primarily to bid you welcome. The University rejoices in the success that this Society has had. It is perfectly conversant with its achievements, and it wishes it every imaginable success, and hopes that in future years its records will surpass those of the years which it has been in existence. Again, on behalf of the Provost and Trustees and all our University family, I bid you the most hearty welcome among us."

THE PRESIDENT: In behalf of this Society, Mr. Vice-Provost, I extend to you our sincere thanks for your cordial welcome to your halls. Five years ago, when we were a mere baby—in fact, even before we had any existence, your University opened its doors to us and bade us welcome, and asked us to hold our first meeting here in your halls. That first meeting was so successful that the formation of the Society was then assured, and I feel that the welcome which the University extended to us at that time was one of the chief features that contributed to the success of the new-born Society. I thank you again, in behalf of the Society, for your kindness.

BUSINESS MEETING OF THE SOCIETY.

The reading of the minutes of the Tenth General Meeting was not called for, and they were approved as published in the Transactions, Volume X.

The report of the Board of Directors, including those of the

Secretary and Treasurer, was presented in printed form to the members, was abstracted by the chairman, and was accepted for publication in the minutes of the meeting, to which it is herewith appended.

The tellers of the annual election presented the result of their canvass of the voting for president, three vice-presidents, three managers, treasurer, and secretary as follows:

REPORT OF TELLERS OF ELECTION.

To the American Electrochemical Society.

GENTLEMEN: We have examined the ballots delivered to us by the Secretary, and report as follows:

Legal ballots	143
Invalid	8
Unidentified	1
Total number cast	152

The ballots were cast as follows:

For President—C. F. Burgess, 112; L. Kahlenberg, 16; Wm. H. Walker, 7; A. H. Cowles, 4; E. F. Roeber, 4. Total, 143.

For Vice-Presidents—C. E. Acker, 108; A. H. Cowles, 88; Wm. H. Walker, 75; S. S. Sadtler, 59; H. S. Carhart, 27; C. M. Hall, 15; C. P. Townsend, 15; A. von Isakovics, 9; S. A. Tucker, 8; C. Hering, 5; E. Weston, 5; E. G. Acheson, 3; L. Kahlenberg, 1; E. F. Roeber, 1. Total, 419.

For Manager—E. F. Roeber, 121; L. Kahlenberg, 74; S. S. Sadtler, 49; F. A. J. Fitzgerald, 40; F. J. Tone, 33; C. M. Hall, 23; H. S. Carhart, 19; W. McA. Johnson, 13; H. B. Coho, 11; A. von Isakovics, 11; W. D. Bancroft, 9; E. G. Acheson, 6; C. J. Reed, 5; C. Hering, 2; C. Mailloux, 1; C. Baskerville, 1; C. F. Chandler, 1. Total, 419.

For Treasurer—Pedro G. Salom, 140.

For Secretary—Jos. W. Richards, 141; S. S. Sadtler, 1.

Yours very respectfully,

ERNST FAHRIG,
FRANK M. OLIVER,
JOHN MEYER, *Chairman.*

President Hering declared the following officers elected for the various terms stated:

President—C. F. Burgess, to serve for one year.

Vice-Presidents—C. E. Acker, A. H. Cowles, Wm. H. Walker, to serve for two years.

Managers—E. F. Roeber, L. Kahlenberg, S. S. Sadtler, to serve for three years.

Treasurer—Pedro G. Salom, to serve for one year.

Secretary—Jos. W. Richards, to serve for one year.

President Hering then called Vice-President Richards to the chair, while he delivered an address, as retiring President, upon the theme, "The American Electrochemical Society," as printed in full, with discussion, in the Transactions, prefacing his address by the following remarks:

"MR. CHAIRMAN, LADIES AND GENTLEMEN: The address of the President this year is somewhat in the nature of a report to the members, and for that reason I have thought best to have it printed and circulated, so that I need not take up the time of this very large meeting to-day to read it in detail. I will bring out the salient points, and, in view of the fact that it is in the nature of a report, with suggestions as to certain future actions, I will submit the address to the meeting for discussion, even though it is not customary to discuss a Presidential address. I feel that this is one of the two occasions we have in a year to get the members together, and I think an expression of opinion from the members on certain points might help to guide the Board of Directors in their actions."

The address was then read, and freely discussed for some minutes; a motion was passed at the close of the discussion to have a mail vote taken to determine the sense of the membership at large upon the proposition of publishing the Transactions of the Society monthly, in the form of a journal published jointly by this Society and the American Chemical Society, the vote being intended as a guide to any action the Board of Directors might contemplate in this matter. For more detailed information, see the Presidential Address and discussion thereon.

Papers by W. F. Mott, C. J. Reed, and Jos. W. Richards were then read and discussed, as printed in full in the Transactions.

Prof. E. F. Smith, of the University of Pennsylvania, then gave a summary, not in the form of a set paper, of the electrochemical work which had recently been accomplished and which is now under way in the electrochemical laboratory of the University of Pennsylvania. The remarks of Dr. Smith were lengthy, and freely discussed. The entire discussion is printed in the Transactions.

After the morning session, members and guests were entertained at luncheon, as guests of the University of Pennsylvania, in Houston Hall, on the University grounds. After luncheon, the chemical and engineering laboratories of the University were opened for inspection.

At 3 P. M. the plant of the United Water Improvement Co., at Thirtieth Street below Locust (ten minutes from the University) was visited. Here was shown the commercial production of ozone electrically, and its use in purifying water; the plant was in operation, and a description of its working, as set forth by the company, is printed at the end of these Transactions.

At 4 P. M. the members and guests visited the lead works of John F. Lewis & Bros. Co., at 2570 East Thompson Street. Here the production of litharge, white lead, red lead, linseed oil, and other interesting paints and pigments was studied in detail.

In the evening, a considerable number of the visitors attended a theater party.

SESSION OF MAY 3d.

The meeting was called to order at 9.30 A. M., in the Lecture Room of the John Harrison Chemical Laboratory, President Carl Hering in the chair.

A paper by G. K. Burgess, an illustrated experimental lecture by C. P. Steinmetz, and papers by W. McA. Johnson (read by title), R. C. Snowdon (abstracted by Prof. W. D. Bancroft), Carl Hering, O. P. Watts (read by C. F. Burgess), and William H. Walker and C. Dill (read by W. H. Walker), were delivered as are published in full in these Transactions.

At 1 P. M., 98 members and guests assembled at Chestnut Street Wharf, on the Delaware, where they boarded the city fire boat "Ashbridge," kindly tendered by the City of Philadelphia, through the Hon. Mayor and the Director of Public Safety. Arriving at Tacony at 2 P. M., the Disston Saw Works was visited, where the manufacture and use of crucible steel was seen; then the Lardner's Point Pumping Station of the Philadelphia Water Works, with its modern steam turbine engines; then the Frankford station of the Philadelphia Electric Co., where Mr. C. J. Russell showed in operation working models of a melting furnace, using Kryptol, an annealing and tempering electric furnace, using fused barium chloride, a miniature Heroult furnace, and a Colby induction furnace in operation, pouring a heat of electric furnace steel, as are all described in a supplement to these Transactions.

Returning to the boat at 3.30 P. M., the party passed along the whole river front, close to Cramp's shipyard, the New York Shipbuilding plant, the Camden By-product Coke Oven plant, the sugar refineries, League Island Navy Yard, and arriving at Gloucester at 4.30 P. M., spent an hour in the extensive factory of the Welsbach Light Co., under the guidance of Mr. H. S. Miner. Re-embarking at 6 P. M., the party was taken to Washington Park, where the landing of the shad nets was seen, and a planked shad dinner was enjoyed from 8 to 10 P. M., at which nearly 100 participated, the largest attended dinner yet held at any meeting of the Society.

SESSION OF MAY 4th.

The meeting opened at 9.30 A. M., in the John Harrison Chemical Laboratory, President Carl Hering in the chair.

Papers by Wilkinson and Gillett (read by Dr. Bancroft), C. F. Burgess, H. E. Patten, Gustav Gin (read by Jos. W. Richards), S. A. Tucker, A. T. Lincoln (Research Subsidized by the Society by $100 grant), Schoch and Hirsch (read by Prof. Schoch), Geo. F. Kunz (read by title), E. R. Taylor, Fitzgerald and Forssell (read by Mr. Fitzgerald), Dr. H. N. Potter, J. Meyer, H. J. Parker, and W. J. Hammer and Goodwin and Mailey (read by title) were communicated, as published in full in the Transactions. Mr. W. G. Morris described a new evaporator—the Kestner, and showed a blue-print of the same. President Hering described briefly the processes of electrolytic refining of gold and silver as practiced at the United States Mint in Philadelphia, which was inspected by the Society later in the day; this description is also appended in the Transactions.

Provost Harrison, of the University of Pennsylvania, greeted the meeting in the following words:

Provost Harrison: "Ladies and Gentlemen: I have come here for a moment to give you a word of welcome, because I was unable to be here on Thursday, when the sessions of the convention opened, for I was called by University duties to the City of New York.

I am very much gratified at hearing from Dr. Smith how full the convention has been and how interesting the papers. I want to say to you, for myself and for the University in general, how glad we are to have the Society here, and I hope that we have been able to make it so agreeable to you that you will want to come here again. You cannot come here too often for us; the oftener you come to the University of Pennsylvania, the more pleasure you will give us.

It happens that while my interest must always be in every department of University work, through particular reasons my interests have been especially in the direction of chemistry.

It is known to you, of course, that this laboratory, while not named after any member of my family which had a direct interest in it, was nevertheless named after my grandfather, John Harrison, who was the first manufacturer of industrial chemicals in the United States of America, and the business which he established has remained in this city until the present day.

The earliest recollections which I have of active life—business life—is trundling a barrow in the chemical works of the Harrison Bros. & Co. (laughter). That was, perhaps, before I was six years old, but I remember it very distinctly.

I have a very great interest, as a family interest, in the question. I wish I could express in clearer words how deep an interest we do feel at the University of Pennsylvania in all scientific bodies which may come here. There are those who are associated with the University who are working for the cause of science in its various subdivisions with great zeal and with great earnestness; and to have a body of men interested in the advancement of one section of the great subject of chemistry come to the University, is a matter in which we feel very great pride.

May I also say that we feel great pride in the Professor of

Chemistry here and in the work that he has done in electrochemistry (applause). He has not only held that position, but holds another relation of equal significance—that is, the friend, and the beloved friend of everyone who is at the University and of everyone who comes to the University (applause).

If these few words of mine, ladies and gentlemen, will make you feel more interested in the University of Pennsylvania and in what we are trying to do here for the cause of science and for other causes, I shall be doubly repaid by the opportunity of having come here to say, at the concluding hours of your meeting, these few words of belated welcome. I will be very much pleased, indeed, to feel that you will very soon come here again; you will, indeed, be always welcome, and we will do the very best in our power to make your stay with us both profitable for the object which brings you here, and personally agreeable to each and every one of you" (applause).

After the withdrawal of Provost Harrison, Vice-Provost Smith took the floor, and said:

"I was very anxious that you should see the Provost of the University, because he has done so much for the furtherance of scientific investigation. We owe to him this laboratory. He paid for it. We owe to him the great Engineering Building, which you visited the other day. He is the man who gave to this University that splendid foundation of $500,000 which has gone into fellowships and new scholarships; and, while his life for thirty years was spent in business—real, active business—if you look around you can see what he has accomplished in the twelve years of his administration of affairs here for the sake of science, literature, etc. I have been laboring all the morning to get him down here, that you might see one who has given from his abundance in this magnificent way—one who is constantly providing for the men who are at work here the means whereby they are able to prosecute their researches, so you will have to take that as my excuse for intruding at this very busy hour, and I know that you will not regret having met one who has done so much for science, although not scientifically trained himself, but a pure art student."

After the reading of the last paper, Mr. E. R. Taylor, seconded by W. J. Hammer, moved the following:

RESOLUTION OF THANKS.

MR. E. R. TAYLOR: I would move the thanks of this Society be extended to John F. Lewis & Bros. Co., Henry Disston & Sons, Incorporated (particularly to their superintendent, Mr. Smith), Philadelphia Electric Co. (particularly to their officials, Messrs. C. J. Russell and W. C. L. Eglin), Welsbach Light Co. (particularly to their chemist, Mr. H. S. Miner), United Water Improvement Co., the various companies who have made exhibits of apparatus at this meeting (Wilson, Mauelen & Co., Eimer & Amend, Leeds & Northrup Co., Kny-Scheerer Co.), His Honor, the Mayor of Philadelphia, and the Director of Public Safety of Philadelphia for facilities furnished for the enjoyable trip upon the Delaware River, the officials of the United States Mint in Philadelphia, (particularly to Dr. D. K. Tuttle and Messrs. Whitehead, Morgan and Slaker), to the Local Committee of the Society in charge of the meeting (particularly to Dr. E. F. Smith, Dr. Taggert, Mr. Chas. E. Reed, and the Registrar, Mr. Goldbaum), and to our host, the University of Pennsylvania, for the place of meeting and its hospitality to the Society.

The motion was passed by acclamation.

Mr. Taylor further stated that, speaking for the visiting ladies, he voiced their appreciation and thanks to the Local Committee and to those who had rendered their visit so enjoyable.

After adjournment there was a demonstration of exhibits in the Chemical Laboratory, followed by a luncheon in Houston Hall, tendered the Society by the University of Pennsylvania (at which some pleasant words of farewell were spoken), and at 2.30 P. M. the Society left for the United States Mint, where an hour was spent in inspecting the electrolytic refining of gold and silver, under the direction of Dr. D. K. Tuttle and his assistants. A brief description of these processes is appended to these transactions.

The visit to the mint concluded the program of the meeting.

ANNUAL REPORT OF THE BOARD OF DIRECTORS.

To The Members of the American Electrochemical Society:

We herewith submit the reports of the Secretary and the Treasurer for the year 1906, the former containing also detailed financial statements.

The financial status of the Society during 1906 was satisfactory, in that the expenditures were brought within the receipts, as was unfortunately not the case in 1905. The receipts and expenditures chargeable to the year 1906 were substantially as follows:

Initiation fees	$ 225.00
Dues for the year 1906	3,095.00
Receipts from transactions and advertisements	594.64
Interest	144.78
	$4,059.42
Expenses	4,053.56
Gain	5.86
Dues for 1906 still unpaid	180.00

The following are the more important actions taken during the year by the Board of Directors:

That members be entitled to insert in the Bulletin of the Society, notices of situations wanted, not to exceed four lines.

Members are invited to furnish discussion of problems announced in the Bulletin, with a view to its ultimate publication in the Transactions.

The Frenzel Prize of $250 was awrded to Gustave Gin, of Paris, for his Essay on "Practical Methods of Treating the Rare Minerals Found in America, and Extracting the Rare Metals Therefrom."

The Society's prize of $100, for original research, was awarded to Prof. A. T. Lincoln, of Urbana, Ill., for research on "The Electrolytic Corrosion of Brass and Special Bronzes."

Since the close of 1906 the following actions have been taken:

That members be allowed a discount of 25 per cent. from the published price, when purchasing the back volumes necessary to complete their sets. Libraries are allowed 10 per cent. discount from their published price for completing sets.

A committee was appointed to confer with a similar committee of the American Chemical Society (already appointed) concerning the proposed joint publication of a "Journal of Physical and Electrochemistry," to be the official organ of this Society, and to contain all its proceedings and Transactions, as well as all papers in this field submitted to the American Chemical Society, and possibly also the incorporation therewith of the "Journal of Physical Chemistry."

CARL HERING, *President,*
S. S. SADTLER, *Secretary.*

Philadelphia, April 6, 1907.

SECRETARY'S ANNUAL REPORT.

FROM MAY 1, 1906, TO MAY 2, 1907.

To the Board of Directors of the American Electrochemical Society:

GENTLEMEN:—I submit herewith the following report on the condition of the Society:

Since the last annual report, the Society has held two general meetings, and the Transactions have been published in Volumes IX and X.

One thousand copies of each volume, bound in cloth, and 500 of each, bound in paper, were printed.

Two hundred and fifty copies of Volumes IX and X have been distributed to members of the Faraday Society, in accordance with the arrangement for free exchange of Transactions.

There were on hand December 31,1905:

335	copies	Vol.	I	cloth.
358	"	Vol.	II	"
242	"	Vol.	III	"
255	"	Vol.	IV	"
240	"	Vol.	IV	paper.
219	"	Vol.	V	cloth.
228	"	Vol.	V	paper.
240	"	Vol.	VI	cloth.
233	"	Vol.	VI	paper.
258	"	Vol.	VII	cloth.
244	"	Vol.	VII	paper.
395	"	Vol.	VIII	cloth.
247	"	Vol.	VIII	paper.
283	"	Vol.	IX	cloth.
251	"	Vol.	IX	paper.

Number of volumes sold during 1903	49
Number of volumes sold during 1904	47
Number of volumes sold during 1905	96
Number of volumes sold during 1906	74

The following data show the condition of the Society in regard to membership:

Total number of members, January 1, 1904	605
Total number of members, January 1, 1905	630
Total number of members, January 1, 1906	631
Total number of members, January 1, 1907	620
Number of applicants elected in 1906	52
Number of resignations during the year	30
Number of deaths	2
Number of members dropped in 1906	31

BALANCE SHEET—DECEMBER 31, 1906.

ABSTRACT OF TRIAL BALANCE			INVENTORY	LOSS	GAIN	ASSETS	LIAB'S	PROFIT AND LOSS ACC'T
Cash	$ 318.94					$ 318.94		
Profit and Loss		$3491.29						$3491 29
Annual Dues		3490.00			$3490.00			
Initiation Fees		255.00			255.00			
Advertising		247.49			247.49			
Expense	2285.64			$2285.64				
Publications	2287.25		$6496.15		3058 90	6496.15		
Interest		144.78			144.78			
Investments	1988.75					1988.75		
Office Furniture	53 00					53 00		
Due from Members	770.22					770.23		
Prepaid by Members		625.24					625.24	
	$8253.80	$8253.80		$2285.64	$7196.17			
BALANCE GAIN				4910.53				4910.53
				$7196.17	$7196.17			
						$9627.07	$ 625 24	
BALANCE—PRESENT PROFIT AND LOSS							9001.82	$8401.82
						$9627.07	$9627 07	

FINANCIAL STATEMENT, JANUARY 1, 1906, to DECEMBER 31, 1906.

RECEIPTS.

From publications (Transactions)	$ 234.20
From advertising	348.36
From initiation fees	255.00
From annual dues	3,564.51
From interest	144.78
Total	$4,546.85

EXPENDITURES.

For publications (Vols. VIII and IX)	$2,352.01
For advertising (commission and expenses)	100.87
For secretary's salary	499.92
For stenographer's salary	372.00
For postage (office and bulletin)	164.66
For postage (Transactions)	241.33
For prize award	100.00
For printing, stationery, insurance, etc.	607.73
New York Section, Ostwald Meeting	50.00
Total	$4,488.52
For Frenzel prize	250.00

CASH ASSETS, JANUARY 1, 1906.

Cash balance, January 1, 1906	$ 260.61
Bonds held by the Society (cost price)	1,988.75
	$2,249.36

CASH ASSETS, DECEMBER 31, 1906.

Cash balance, December 31, 1906	$ 318.94
Bonds held by the Society (cost price)	1,988.75
	$2,307.69
Gain in cash assets for the year 1906	$ 58.33

Two volumes of Transactions, namely, Volumes IX and X, have been published since the last annual meeting. Volume IX contains the papers read at the Annual Meeting of the Society, held in Ithaca, N. Y., May 1, 2 and 3, 1906; Volume X contains the papers read at the Tenth General Meeting of the Society, held in New York, N. Y., October 8 and 9, 1906. This volume was smaller than usual, because the meeting was of only two days' duration instead of three as heretofore.

Forty-seven papers were printed in the Transactions in 1906, as compared with forty-two in 1902, forty-five in 1903, forty-four in 1904, and fifty-three in 1905.

I find that the Transactions of the Faraday Society are much appreciated by our members, and all expressions from England have shown a similar appreciation of our Transactions by members of the Faraday Society.

The membership in 1906 was slightly reduced, owing to the enforcement by the Board of the provisions of the Constitution concerning the dropping of members for non-payment of dues.

The financial condition during the year 1906 was satisfactory, in that the expenses were within the receipts, while in 1905 the expenses appreciably exceeded the receipts.

S. S. Sadtler,
Secretary.

Philadelphia, April 6, 1907.

TREASURER'S ANNUAL REPORT.

YEAR ENDING DECEMBER 31, 1906.

Jan. 1, 1906—Balance	$ 505.72	
Jan. 1st to Dec. 31st—Receipts	4,448.56	
		$4,954.28
Jan. 1st to Dec. 31st—Expenditures as per vouchers Nos. 61 to 135, inclusive		4,635.34
Cash balance December 31, 1906		$ 318.94

Pedro G. Salom,
Treasurer.

MEMBERS ELECTED AND QUALIFIED.

JANUARY-JUNE, 1907.

January 5, 1907: B. B. Burling, Lancaster, N. Y.; Prof. C. L. Speyers, New Brunswick, N. J.; Harry P. Wood, Urbana, Ill.

February 2, 1907: S. T. H. Hall, Helena, Mont.; H. Henry Lienau, New York City.

March 2, 1907: R. D. Thomas, Oakmont, Pa.; C. H. Kerr, Niagara Falls, N. Y.

April 6, 1907: Dr. Wm. McMurtie, New York City; Tracy D. Waring, Perth Amboy, N. J.; R. W. Lohman, Oakland, Cal.; H. B. North, Madison, Wis.; J. L. Harper, Niagara Falls, N. Y.

May 2, 1907: Wm. Honey, Tequisquiapan, Mexico; Harlan S. Miner, Gloucester, N. J.

June 1, 1907: Allerton S. Cushman, Washington, D. C.; Royd R. Sayers, Bloomington, Ind.; John F. Hammond, Prince Bay, N. Y.; J. D. Du Faur, Mt. Morgan, Sydney, Australia; John L. Tufts, Worcester, Mass.; W. M. Grosvenor, New York City; J. Forssell, Cleveland, O.; Jos. B. Crane, Schenectady, N. Y.; J. F. Queeny, St. Louis, Mo.; F. W. Liepsner, Columbia, Mo.; C. F. Lindsay, Schenectady, N. Y.; Roger C. Wells, Schenectady; George A. Richard, Mt. Morgan, Australia; A. H. Pikler, Montclair, N. J.; S. Skowronski, Perth Amboy, N. J.

June 29, 1907: W. E. F. Bradley, New York City; L. M. Willey, Schenectady, N. Y.; W. R. Ingalls, New York City; H. R. Moody, New York City; I. Langmuir, New York City; A. Hirsch, Corpus Christi, Tex.; Dr. Fritz Zimmermann, Newark, N. J.; H. McCormack, Chicago, Ill.; M. Medove, Newark, N. J.; H. Casselberry, Altoona, Pa.; Dr. Heinrich Wohswill, Hamburg, Germany.

An address delivered at the Eleventh General Meeting of the American Electrochemical Society, held in Philadelphia, Pa., May 2, 1907, Vice-President J. W. Richards in the chair.

[PRESIDENTIAL ADDRESS.]

THE AMERICAN ELECTROCHEMICAL SOCIETY.

BY CARL HERING.

The present meeting closing, as it does, the fifth year of the existence of this Society, and being held in the city of its birth, even in the very halls in which its eminently successful inaugural meeting was held, was thought to be an appropriate occasion for addressing the members on a subject which cannot fail to be of interest to all, namely, on the Society itself, its past, present and particularly its future.

Modern societies are usually conducted by a few of their members, sometimes by a very few, who, as the chosen directors, relieve the general meetings and the membership at large of nearly all matters of society business, thereby enabling the meetings to be devoted entirely to papers and discussions, and avoiding the dissensions, division into factions, and snap legislation which are so likely to occur when the business matters of a large, and especially a national society, are transacted by the small percentage of members present at a general meeting. But the directors thereby have heavy burdens placed upon them in the form of grave responsibilities; the failure or success of the whole society often rests with them. It is impossible for a few to always please everybody, but it is a great pleasure to be able to say that during its whole short history our Society has so far been free—I can even say absolutely free—from any serious dissensions, factions, or any unpleasant disputes of any kind—a record which we can all feel proud of and which, let us all hope, may continue.

Although the government of a society by a few directors has great advantages and is, no doubt, the most satisfactory method, yet it has the one disadvantage that the members do not become familiar with the vital business affairs of the society, they are, in fact, even likely to take no interest in them, sometimes, perhaps, to their own and the society's loss.

For this and other reasons, it is hoped that no apology need be offered by your retiring President for taking advantage of this occasion to say a few words to the members about their own Society, after a five years' service on its Board of Directors. Matters of great and even vital importance to the welfare of the Society may soon arise, which the members may have to decide, and it was thought that a brief summary of its past, present and possible future, may help them to do so more intelligently. Some important changes are already in sight, such, for instance, as the reduction of expenses or raising of dues, combining with the American Chemical Society in the issue of a joint publication, the question of holding only one meeting a year or continuing to hold two, the ultimate removal of headquarters to New York City, the financial support of local sections, etc.

It seems to the writer that all such questions concerning the future can be more intelligently discussed and decided by first studying the past and present. An individual may take chances in deciding upon making changes concerning his own welfare, but it may result seriously for a society to do much experimenting with itself. Its inertia is greater than that of an individual; it requires great efforts to bring it back into the right path again, if a change in the wrong direction has been made; hence proposed changes should be well considered before they are made.

The history of the formation of the Society is brief. A little coterie of three of its present members interested in electrochemistry had met at each others homes here in Philadelphia, for several years, to discuss problems arising in this branch of science, and the discussions proved so interesting that it was suggested to form a national society, by which all the best work of this country could be collected, discussed and published. A call was issued to about 30 persons, who were thought to be interested in the subject, resulting in a preliminary meeting at the Engineers' Club of Philadelphia, on November 1, 1901, attended by 11, of which a large percentage was from out of town. It was there decided that if the names of 75 could be obtained who would pledge themselves to become members, the Society should be formed. Committees were appointed to draw up a constitution and arrange for the first meeting. The response to this call was so unexpectedly great, 337 membership pledges being received from 36 States and 8 foreign countries, that success was assured, and, as a result, the Society was formed at the organization meeting held at the Manufacturers' Club on April 3, 1902. attended by 52 of the charter members, followed by a three days' meeting at this University, which, to-day, stands as one of the most interesting meetings ever held by this Society.

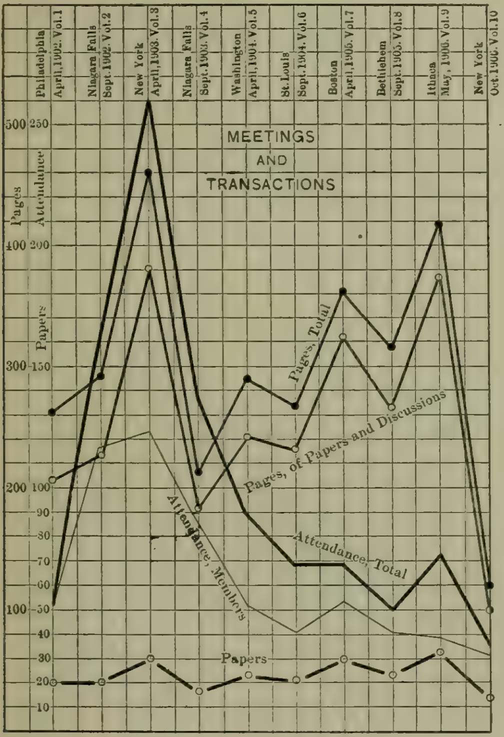

FIG. 1.

In order to show its history for the last five years briefly and concisely, I have prepared the following curve sheets, which show more, at a glance, than pages of tables and text. The first one (Fig. 1) gives the data of the meetings and the Transactions. It is self-explanatory and needs no further description, but some comments on it may be of interest. In such saw-teeth diagrams, one should not attach too much importance to abnormal peaks or depressions, but observe rather the general trend of the average curves. The first New York meeting, in 1903, for instance, was held under exceptionally favorable circumstances, and the second one, in 1906, under exceptionally unfavorable ones; both are abnormal; we should not be discouraged at not being able to keep up the record of the former, as that would be impossible; nor should it be assumed that the last meeting is an indication of the future.

In general, the trend of the curves of both sheets is toward a normal, showing that the wide fluctuations which are to be expected when a new society is started, are lessening, and things are apparently beginning to assume their natural levels. It therefore becomes possible now to look ahead and predict the future with a more secure feeling than it was during the periods of great fluctuations.

Omitting those two exceptional meetings, the curve of the amount of matter in our Transactions, which is, perhaps, the best indication of whether there has been progress or decline, shows a general and healthy rise, as does also the curve of the number of papers. The regular saw-tooth nature of the curves show that our spring meetings have always been better than those in the fall. The curve of the attendance is not so satisfactory, but again omitting the two abnormal meetings in New York, it shows a tendency to assume a normal level. The attendance at the first few meetings has not been maintained, but this was to be expected, as special efforts were made at those introductory meetings to acquaint persons with the work of the Society. This cannot be expected to be kept up; we are now assuming a normal, which, it is hoped, will be maintained and be gradually and permanently raised. It will be noticed that the abnormally great attendance at the first New York meeting was due almost entirely to the large number of guests, and the apparent fall at the last meeting to the absence of guests, or perhaps only to their failure to register. The attendance of the members themselves is the more important of these two curves.

The second curve sheet (Fig. 2) shows the data concerning the membership and the finances. Neglecting the two small peaks, due to the method of keeping the records, the curve for the membership tends toward a horizontal. What slight fall there is, is probably accounted for by the recent clearing out of dead wood in the form of delinquent members, some of whom should perhaps have been dropped earlier. The curve showing the acquisition of new members, is also assuming a level and is gradually meeting the curve showing the loss of members. It has, in fact, crossed it already, but, as just stated, this is due to keeping delinquent members on our rolls too long.

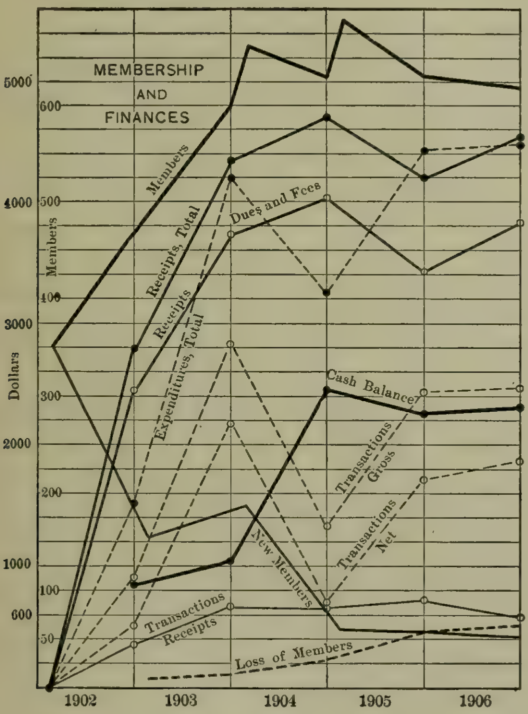

FIG. 2.

The curves showing the total receipts and expenditures also tend to a level. The abrupt bends in these curves are due largely to the fact that expenditures contracted during one calendar year are sometimes paid in the next. But, neglecting these local irregularities, the two curves have been getting closer and closer together and are now quite near to each other. In 1905, the expenses increased very rapidly, and the receipts fell considerably; the two lines even crossed, showing that the expenses had exceeded the receipts, but, by close economy last year, they have again been crossed over to their former and proper relative positions. The income also decreased materially in 1905, but it is now again on the rise and points in the right direction. Although the expenses have been brought within the receipts again during the past year by careful economy, they are closer than they should be, and the general trend of the two curves is to cross again in the near future, from which we should take warning in time.

The curve of the cost of the Transactions is also seen to be assuming a normal level again, after a rapid increase during 1905. It will fall during this year owing to the present volume being smaller than the average.

The cash balance curve is also assuming a level again; in fact has even risen slightly during the last year after an appreciable fall during 1905. The rapid growth of this cash balance during the first three years was virtually a gift from our former secretary and founder member, Mr. C. J. Reed, as he refused to accept a salary for his very energetic, able and conscientious services; since we have paid a salary to the secretary the cash balance has ceased growing. This cash balance is quite large for such a young Society, and gives it a good financial standing. It is, however, not entirely a net asset, as the cost of one volume of the Transactions is always chargeable against it, being paid the year following. But we are accumulating another and probably still larger asset in the form of the copies of the Transactions in excess of those given to the members. These have been paid for and are being sold in quite appreciable numbers each year.

In the above financial data the Frenzel prize of $250 has been eliminated entirely, and the bonds have been considered as cash at their purchase price. These data, therefore, show the true financial affairs more clearly than the treasurer's annual reports.

My analysis of the affairs of the Society to see where improvements might be possible, revealed a somewhat curious state of affairs. Dividing the annual expenditures by the number of members, shows that what the Society has done for its members for the last five years has cost it $6.05 per member per year, and for this a member pays only $5.00 dues. In other words, a member of this Society seems to get more than what he pays for; this ought to be an inducement for others to join. During one year this figure even reached $7.24, and during another $7.03. And yet, during those five years, we have accumulated a handsome cash balance of over $2,000, and a still greater asset in a stock of salable volumes of Transactions, estimated at about $6,000. This apparent paradox is explained, in part, by the fact that the initiation fees have been used to pay a part of this deficit; but this is not good financiering; as the number of new members per year is diminishing, this source of income is decreasing proportionately. The other source of income, which, in part, pays this deficit, is the sale of back numbers of the Transactions. This has been fairly constant at about $600 per year, or nearly $1.00 per member; as this proves to be an essential part of our income, it must be carefully considered in any negotiations concerning joint publications. If we cease publishing our own Transactions, this income will either cease or at least greatly diminish, and the large asset which we have accumulated in the form of a stock of back numbers of the Transactions will become practically valueless, as there is little demand for the back numbers of a serial publication which has ceased being published.

Although the curves showing the finances took decided turns in the wrong direction in 1905, and gave just cause for alarm, it is reassuring to see that during 1906 they were righted again, and are now tending to go in the right directions. While this is a comfortable feeling, we should take a lesson from the past and not let our vigilance relax.

In connection with the growth of our Society, it is of interest to make a comparison with that of the only other national electrochemical societies, namely the older Bunsen Society, in Germany, and the younger Faraday Society, in England. The adjoining diagram, Fig. 3, gives the ages and present membership of all three and the inclinations of the lines show the average rate of growth of each up to this year. It will be seen that ours has grown more rapidly than either of the others, and is nearly as large as its older sister society. Whether these rates will continue is mere conjecture, but if they do, our Society will, in the near future, be the largest of them all.

Having glanced over the past, let us take up briefly the problems of the immediate future.

The question of the raising of dues is perhaps the one of most general interest. In 1905, the finances pointed strongly to the imperative necessity in the near future of either an increase in dues or a decided reduction in expenses by the omission of one of our two yearly meetings. But it has been shown above that, by strict economy, these financial curves have been turned in their right direction again during 1906, and it is the opinion of your president that, by continuing to exercise strict economy, there is no immediate necessity to either raise the dues or to drop one meeting, provided, of course, that no radical changes are made. It seems, therefore, that we may still continue to enjoy the reputation of giving to our members more for such low dues than any other national society in this country or perhaps even in the world.

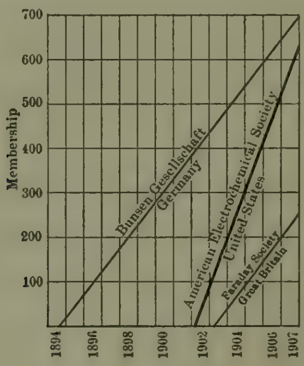

FIG. 3.

The question of abandoning one meeting a year, no longer seems to be a necessity for avoiding the raising of the dues. It is now only a question of whether we can get material enough for two meetings. Until the last meeting, we have generally had more papers than we had time to discuss properly, and without discussions the meetings lose in interest and value. It, therefore, does not seem now as though a scarcity of papers is to be feared, especially as this industry and science are growing. By holding only one meeting we would be sure to lose valuable material that would otherwise come to us, because when a member has something of interest ready, it is not likely that he would want to wait, perhaps the greater part of a year, before making it public; he would most probably read it before some other society or give it to the press. If, however, it should become advisable to reduce the meetings, the plan which I have advocated is to try a mean between the two, that is, to let our large spring meeting be the important one and then hold a less pretentious and perhaps shorter meeting in the fall, in a central location like New York City, where there is a large local section and a large local membership. It might, perhaps, be held under the auspices of the local section. The last meeting in New York City was intended to be a test of this plan, but, unfortunately, it was encumbered by a number of mishaps, which it would be unjust to assume to represent normal conditions and it therefore cannot be taken as a normal and decisive test. I would urge trying it again next fall and getting the large and active New York local section to assume the responsibility of its success. To omit one meeting entirely would, in my opinion, be the beginning of the decadence of the Society, resulting ultimately in our absorption by some larger society. By far the greater number of our members have joined for the sake of the Transactions, and many of these would, no doubt, be unwilling to pay the dues for only one volume. Our Transactions are one of our chief attractions and assets, and they should be guarded zealously.

The question of the ultimate removal of our headquarters to New York City, as was originally contemplated by the founders, seems to have been settled for the present by Prof. J. W. Richards' acceptance of the secretaryship, which, naturally, involves the removal of the headquarters to Bethlehem. The question of the cost of headquarters in New York City was considered by the present administration, and it was found that the increase of expenses would be so great that an increase of dues at once would become inevitable. It is not thought that the advantage to the members at large would warrant such an increase of their dues.

The question of the financial support of local sections was also raised during the past year. There are at present three such sections, New York, Philadelphia and Madison. The two latter are necessarily small, and have never asked for or received any financial support from the Society's treasury. It is against our present rules to grant such support, and unless the differences between our income and expenses grow rapidly, which is not likely, no money can be spared for supporting local sections. The support of one would necessarily involve the support of all, both at present and in the future. Such local sections, however, should be encouraged in all national societies, and anything that the Society is able to do for them should be done. The simplest and most just way would seem to be to collect, say $6.00 dues, instead of $5.00, from those who are members of local sections, and then pay over to each section the extra dollar per member. In this way the members at large cannot complain that they are being taxed to pay for the maintenance of local sections from which they derive no benefit. Papers read before local sections could, however, be published in the Transactions at the Society's expense without fear of such a complaint, as all members then get the advantage of those papers and discussions.

A matter of considerable interest to the Society has been brought up recently in the form of a tentative proposition from the American Chemical Society, originated by Dr. W. A. Noyes. Briefly stated, the two basic features of the proposition are, first, to combine into one monthly publication all papers on physical chemistry and electrochemistry read before either society, and second, to reduce the cost of the publications of both societies by having the work done by one publication board. It is proposed, also, to combine the *Journal of Physical Chemistry* with this new joint publication.

It is, I presume, needless to say that such a co-operation would be of great benefit to all concerned and is highly desirable. To have the work of publishing done by one board for both societies would naturally reduce the expenses of both, as it avoids the duplication of expenses, gives both the advantages of cheaper rates and involves the principle that the cost of an additional amount of work is generally less in proportion. It therefore seems hardly necessary to dwell on the self-evident advantages of this feature, especially in the present era in which the combination of joint interests to reduce expenses is the prevailing practice.

The advantages of combining into one publication all papers on these two almost inseparable subjects, which are read before either society, and at the same time combining with it the *Journal of Physical Chemistry,* are also so self-evident that it seems hardly necessary to call attention to them. It is estimated that the amount of matter in it would probably be about double that of our Transactions. Not only would such a publication be of more value to those who get it, than any of its constituents would be; not only would it bring together all the papers on the same general subject under one cover, but it would also avoid the duplication of the same paper in the different publications, it would give each paper a wider circulation, and would, in the future, facilitate the searches for published information on this general subject and making references thereto. Incidentally, and fortunately, it might be added, that as there is no keen rivalry between the present publications no one would be the loser.

A combination of interests, in which all parties gain and no one loses, is certainly one which should be brought about if possible. The question, therefore is not so much whether it *should* be done, but whether it *can* be done; in other words, can such an arrangement between the parties be reached? There were mentioned above only the two basic features of such a joint publication; there are necessarily involved many others, which make the problem a somewhat complexed one. One of the important, and perhaps the most important, is, how should the expenses be divided? Another is, would not such a combination of publications reduce the membership of the societies by those, numbering at present about 200, who are now members of both societies, and would not this loss fall entirely on our Society. Another is, should it be published jointly by both, or by the Chemical Society as originally proposed.

After numerous and long conferences with some prominent representatives of both societies and with the editor of a similar joint publication, and after careful consideration of the subject, your President believes that, to be acceptable to all parties involved and to be lasting, such an agreement must be based on the following fundamental conditions:

1. It must be equitable to all concerned, neither party receiving any advantages at the expense of the other, and neither party assuming risks which the other should share. Things that are

likely to cause discord should be eliminated at the start as far as possible.

2. To be permanent, the division of expenses for the future should not be based on present conditions. Societies change; they have their ups and downs; it would be highly improbable that the proportion of members and papers to-day in the two societies would remain the same for years to come. Societies are not individuals, and it is an important question in how far we to-day have a moral right to bind our successors. It therefore seems that, to be as equitable in the uncertain future as it is in the certain present, such an agreement must be co-operative in the true sense of the word; the division of expenses should be such that it will be as equitable under changed conditions as it is to-day; under no other conditions would it be likely to last; and a temporary break in the succession of the publications ot a society is too serious a matter to be experimented with.

3. That the individuality and independence of the two societies should not be affected by such a joint publication of their papers.

It seems to your President that a general plan, briefly outlined as follows, and based entirely on business principles, would meet these conditions. There is a wise proverb that strict accounts keep up a good friendship. Many a friendship has been destroyed by loose or unjust accounts between the parties.

That the two societies jointly organize a Bureau of Publication, which is to receive all the material for all the publications of both societies when it is ready to be printed. Each society is to collect, edit and prepare for publication the papers, discussions, abstracts, etc., contributed by it, and at its own expense. The Bureau ot Publication shall then print the same and supply each society, or its members, with the number of copies asked for. The expenses of the Bureau should be divided into three parts: *a,* those for typesetting, cuts, inserts, etc., which are in proportion to the amount of matter contributed by each society; *b,* those for printing, binding, mailing, etc., which are proportional to the number of copies printed; *c,* those which are general. Each society should then pay its proportion of *a,* as shown by the amount of matter contributed; its proportion of *b,* as shown by the number of copies asked for; and the general expenses, *c,* should then be divided in the same proportion as the sum of these two. The representation on the Board might each year be in proportion to this division of expenses of the previous year.

With such a division of expenses, the proportions will be equitable, and will adjust themselves without friction during all times to come, no matter how the societies may change. The American Chemical Society would thereby be assuming the entire expense of its own Journal and of its Abstract Journal, to which our Society contributes no material, and we would bear the entire cost of our Transactions, if that society should contribute no papers on electrochemistry or physical chemistry. The expenses to each society, however, would be less than they are now, due to the combined management. Each society would then, at all times, pay its appropriate share of the cost, in exact proportion to what the Bureau does for it, be it much or little. Neither party would assume risks which the other should share, and the same is true of any gains. If both societies were to have this joint publication printed by a disinterested publisher who is in that business, he would probably divide the charges in the proportions above suggested. At present, the costs of the publications of the two societies are paid for in this same proportion, and the only change therefore would be that the amount would become less, but in the same proportion, while at the time time the publication would be greatly enlarged.

If it could be assumed that now and in the future our papers would always be so acceptable to the other society that it would be glad to pay for the typesetting and cuts of all our papers, and we pay for theirs, as has been suggested, this division of this item of the expenses might be reversed. But it seems to me that this might be an unsafe assumption to make for an indefinite time in the future. We would be pleased to know that this is so to-day, but is it safe to base a long term agreement on the assumption that it will always be so? The natural result would be that some time, sooner or later, one or the other society would want the right of censorship over the papers of the other society before it is willing to pay for publishing them. This would mean a loss of independence. A paper which is very expensive, due to length, cuts or tabulated matter, and perhaps of questionable value, would be likely to give rise to a dispute. But if each society continue to pay for its own papers, as it does now, such disputes cannot arise; each society will then maintain its independence and neither will have the right of censorship over the other. Losses would be shared.

If, however, it is thought that the first-mentioned and strictly equitable method of dividing the expenses is too cumbersome, although it is only a simple matter of bookkeeping, I would suggest that the total expenses of the joint publication be divided between the two societies in proportion to the number of copies taken by each. The questions of censorship and expensive papers will then have to be met in some other way when they arise.

Many other features are necessarily involved in such a long-time contract, but they are of a minor nature and seem to be easily adjusted if the basic conditions, outlined above, are agreed upon. We can then, for instance, continue our exchange of Transactions with the Faraday Society, and at a lower cost, even though we will be giving that society additional literature. We can keep up our valuable asset of a supply of back numbers for future members, and our independence will be maintained. In short, everything seems to remain the same as it is now, except that each society gives its members a larger amount of matter in its publications, and at less cost than at present.

The almost certain loss of some members who now belong to both societies is, it seems, the only feature on the other side of the balance sheet. There are now about 200 who belong to this class. This loss may, perhaps, be divided between the two societies, but it is likely to fall almost entirely on us. It will be partially, and may, perhaps, be completely counteracted by an increase in new members, as a member in our Society will then be getting still more for his small dues, notwithstanding that he is probably already getting more per dollar than in any other society. It is proposed, also, that the members of each society should then be able to purchase the Transactions of the other at a reduced rate, but it will necessarily be obligatory then to provide that the price shall not be less than a certain minimum, otherwise one or the other society would soon become extinct, and, as we are to-day the smaller of the two, we would be the one to suffer.

It might be added here that there is already in existence, and has been for over twenty years, a somewhat similar co-operation of various engineering societies to publish their Transactions jointly. An organization was formed, called the Association of Engineering Societies, whose function is to publish in one journal the transactions of about 11 local engineering societies. Its experiences might serve as a useful guide in the formation of a somewhat similar, though not identical, agreement.

In the opinion of the writer, the surest way to reach an agreement which would be as equitable in the future as it may be to-day, is to consider this publication board as an outside and disinterested party, like a publishing house, which collects its charges from the two societies in a just and fair proportion to what it does for each. The fact that the proportion of the number of pages printed for each is not, or may not be in the future, the same proportion as the number of copies taken by each, complicates the division of the expenses, but as the pro-rata method outlined above is based on both of these proportions, it cannot fail to be just to each, and, in fact, seems to me to be the only proper method which conforms itself as well to the unknown conditions of the future as to the known conditions of to-day.

Perhaps we might venture to go a step farther and join with still more societies to form a joint publication bureau, which is to publish all of their transactions, a large, general, publication bureau. If the question of the proper division of expenses should form an insurmountable obstacle in the desirable object of joining our publications, a practical solution of the problem would be to let some reliable existing publishing house take the place of this proposed joint bureau, and let it divide the expenses according to business principles. The objection to this might be that the charges for its services might more than balance the savings due to co-operation. Another method of settling this difficult question of the proper division of expenses would be to jointly agree on some disinterested publisher who shall decide how the division should be made.

But whatever arrangements may be made, I think you will all agree with me on the following:

That such a combination of publications is of mutual advantage, is very desirable and should be accomplished if possible.

That if entered into, it should be done with the view of permanency and not as an experiment, and that, therefore, the arrangements should be such that they will be as equitable in the future under changed conditions as they are to-day.

That we should not thereby lose our independence or subject our papers to the censorship of any other society.

And that it should not jeopardize the future existence of this society.

I might add that, according to our constitution, the Board of Directors has the right to enter into such a contract without submitting the question to the members, and it is therefore desirable to discuss the question with the members at some general meeting like the present.

Formerly, our Society was liberally entertained in the cities in which it held its meetings, by funds raised by the local members. While such entertainment has added greatly to the enjoyment and attractiveness of the meetings, it has been felt for some time past that the Society ought not in the future to allow itself to impose this burden on the local members, especially in the smaller cities. It was therefore thought by a number of members that it would be well to establish, in part at least, at this meeting, the precedent that the society and its members will entertain themselves, and that they ask of the local committees only to arrange a program which will enable them to do so. This, it is thought, would make all feel comfortable, and would no doubt tend to increase the feeling of welcome which has always been extended to us in the past. Notwithstanding the intentions to establish this precedent at the present meeting, several invitations on the program were so cordially offered and volunteered, that exceptions were made in those cases.

Appended to this address are given the numerical data corresponding to the curve sheets above mentioned.

Before passing the Presidency to my successor, I wish to thank you all for the courtesies extended to me during the past year, and I sincerely hope that the good work of this Society, the mutual benefit of its members, and the interest in it, which its original founders strove to develop, may continue to be maintained and to increase.

TABLE I.—MEETINGS AND TRANSACTIONS.

	Numbers of meetings and volumes of transactions.	ATTENDANCE.			TRANSACTIONS.		
		Members.	Guests.	Total.	Papers.	Pages of papers and discussions.	Total number of pages.
Philadelphia, April, 1902 .	1	52	. . .	52	20	206	262
Niagara Falls, Sept., 1902 .	2	117	47	164	21	228	292
New York, April, 1903 . .	3	122	138	260	30	382	460
Niagara Falls, Sept., 1903 .	4	186	53	139	17	184	212
Washington, April, 1904 . .	5	52	38	90	23	244	298
St. Louis, Sept., 1904 . . .	6	41	21	69	21	234	268
Boston, April, 1905	7	53	16	69	30	326	362
Bethlehem, Sept., 1905 . .	8	41	9	50	24	268	316
Ithaca, May, 1906	9	39	33	72	33	374	416
New York, Oct., 1906 . . .	10	32	6	38	15	100	148
Totals	10	635	361	1003	234	2546	3034
Average	[illegible]	63.5	36.1	100.3	23.4	254.6	303.4

TABLE II.—MEMBERSHIP.

	Members	Elected	Resigned	Died	Dropped
April 3, 1902 (Charter Members)	350	350	. .	. .	. .
April 16, 1903	492	152	5	5	0
January 1, 1904	605	. .	. .	. .	. .
April, 1904	661	186	15	2	0
January 1, 1905 . . .	630	. .	. .	. .	. .
April, 1905	689	60	28	4	0
January 1, 1906	631	57	24	6	26
January 1, 1907	620	52	30	2	31

TABLE III.—FINANCES.

	RECEIPTS			EXPENSES		Gain and Loss	Cash Balance at End of Year
	Total	Dues and Init. Fee	Transactions	Total	Transactions		
1902	$ 2787.47	$ 2429.60	$ 344.20	$ 1907.98	$ 848.31	+$879.49	$ 879.49
1903	4342.35	3700.00	642.35	4196.32	2793.96	+ 146.03	1025.52
1904	4700.20	4029.12	659.47	3251.77	1318.20	+1448.43	2473.95
1905	4205.89	3413.31	716.34	4430.48	2408.98	— 224.59	2249.36
1906	4546.85	3819.51	582.56	4488.52	2452.88	+ 58.33	2307.69
Totals	$20582.76	$17391.54	$2944.92	$18275.07	$9822.33	+2307.69	$2307.69
Av'ge	$4116.55	$3478.31	$588.98	$3655.01	$1964.47	+$461.54	$461.54

DISCUSSION.

PROF. J. W. RICHARDS: We have listened with great interest to the many fruitful suggestions in the retiring president's address, and, at his especial request, call for discussion upon the points which have been raised. I therefore declare the meeting open for discussion, for any who wish to take part in it, on any of the topics which have been brought up, particularly that of the possibility of making a combination of publications, if such could be practically and equitably arranged.

PROF. BANCROFT: It seems rather a thankless thing to do to criticize this report, but we have been asked to do it, so I might as well throw myself into the breach.

Mr. Hering and I agree heartily and in every respect, so far as I know, as to what ought to be done. Mr. Hering thinks that the only requisite for two meetings a year is to have enough papers. My opinion is that the difficulty is more as regards the men; that it is too much of an expense to the people who come to the meetings. If we cannot hold two meetings a year, we cannot publish two volumes of Transactions; and if we do not publish two volumes of Transactions, our membership will fall off very rapidly, because not over three or four per cent. of the members come to the meetings. To my mind the situation is critical, and I think that this suggestion of joint publication is a very desirable one, which comes to us rather in the nick of time.

But here again we differ on what is to be considered good business. Mr. Hering's plan is that we should pay exactly in proportion for what we furnish, which, of course, has certain obvious merits. It has the distinct and obvious demerit that it might easily happen at some time that our share of the expense was greater than our actual receipts. Our present expenses run pretty close to our actual receipts, and it seems to me that it would be well to guard against over-running in some way. Then there is another point, in regard to the distribution of expenses, which Mr. Hering overlooks completely, and that is that in the Chemical Society, so-called, a great many papers are sent to the Journal and are published in the Journal which are not presented at the meetings at all, and it is going to make a great deal of difficulty, purely as a bookkeeping matter, to find out where those things are going to come in.

Of course, you can say that they are to be attributed to the members of the society who furnish them. The weak point about that is that at the Ithaca Meeting, at any rate (which was the last meeting for which we have printed Transactions), over 80 per cent. of the actual papers were supplied, directly or indirectly, by men who were members both of the Chemical Society and the Electrochemical Society, so that you have a pleasing bookkeeping snarl. It can be gotten around; anything of that sort can be gotten around. The question is one whether the offer that was made is not really the better one. The tentative offer made by the Chemical Society was that we should have the joint publication, that we appoint two members of the board of editors, that we should pay a fixed sum—$2 a year per member—which should cover the whole of our expenses in connection with the publication.

Under these circumstances we cannot lose money, because our expenditures for publication cannot exceed 40 per cent. of our total receipts in a year. That, it seems to me, is a distinct advantage. Incidentally, they also offer to pay us a small sum—25 cents a member—for those members of their society who take the joint publication and who are not members of the Electrochemical Society, so that we also get in a slight income there.

Now, it seems to me to meet everything. We are guaranteed against loss. If we wish to publish a lot of papers, we are perfectly safe. If we are doomed to dwindle away and die (which I do not believe is the case), we are also safe (laughter). Well, I'll put it slightly differently—under those circumstances we can still die gracefully.

Mr. Hering has laid a great deal of stress on the point that if one side cannot lose, the other side must. Now that is not quite a fair statement, from my point of view. It is quite conceivable that under certain circumstances what we pay towards publication may not actually cover the cost of publishing the number of pages which we contribute, but it does not follow, from all that, that the Chemical Society is losing by the bargain, because there are a great many other factors. The Chemical Society gains from this transaction, because they get all the physical chemistry and electrochemistry published under their auspices, whereas now a great deal of it is published independently. We gain, because we get all the electrochemistry published together. The estimate that it will double what we are able to furnish to our members is an under-estimate. As a matter of fact, we shall be able to furnish a great deal more than twice what we are getting now. A great deal of the electrochemical work is now published in the Journal of the Chemical Society, and we don't get it. Under the proposed arrangement, we shall get the whole of it; we shall be able to give our members twice as much reading matter as we do now; we are guaranteed absolutely against financial loss, and, consequently, all we have got to do under those circumstances is to concentrate our efforts on seeing that we are not gradually absorbed. So far as I can see, this is one of those ideal things where everybody gains a great deal and nobody loses anything, and it seems to me that it is pretty good business, and that we had much better accept an offer like this than the plan outlined by Mr. Hering.

President Hering: I did not neglect to consider those papers which are simply handed in, but are not read at a meeting; they are taken care of. As to the accounting, if we could not do that small amount of bookkeeping, we could hire an amateur bookkeeper for a small sum of money who will be able to keep those accounts straight. The cost of $3 per member* is much more than we are now paying for our Transactions, so that we would be paying them considerably more for the Transactions than they are costing us now, and it must not be forgotten that in printing our own Transactions we are accumulating back numbers; we are making an investment which yields us about $600 a year, and is, therefore, not to be overlooked. If we paid them $3 a member, we would pay them nearly $1,900, while the Transactions now cost us only about $1,300, net; so you see, we would be paying them more than we are paying now.

Mr. Reed: It seems to me that any action of this kind should not be taken by the Board of Directors without the authority of the Society, for the reason that the directors could not make any arrangement which would be binding for more than one year. It might be repudiated the next year by the incoming Board of Directors, with disastrous results.

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*Subsequently reduced to $2 in a letter received too late to be read at this meeting. C. H.

Dr. Doremus: It seems to me that it would be advisable to consider our exchange with the Faraday Society. It has been a matter of very considerable pleasure to many of us to think that we are exchanging Transactions with that body. There ought to be something provided for, for the continuance of that friendly relationship.

President Hering: According to the proposed plan, this could be continued the same as at present, and it would cost us no more than it does now. In fact, it would cost us a little less, and we would be giving the Faraday Society much more material for less money.

Mr. Isakovics: I am afraid that under these conditions we would not grow very fast, and I am afraid we would lose more members than we would gain. Our best argument in the getting of new members has been the Transactions themselves, and I think that if we do not publish them ourselves we will lose the opportunity of getting many members.

I think the conditions which Mr. Hering outlined are ideal, but I am afraid that there are so many uncertainties involved in the change that we ought to think it over a few years before making it. So far, there has been no deficit in our finances, the Society is growing, and I think it will continue to grow, but under this proposed new plan I think we would lose at least about one-third of our membership in the next two years. A great many of the members that belong to the two societies would, I think, drop this one, and the new conditions would make it very hard to get in new members.

President Hering: It may be of interest, in this connection, to say that there are about 200 of our members who are also members of the American Chemical Society. If we should lose all these, we would be losing 200 out of 600.

Mr. Carrier: I do not understand whether the plan is to publish our Transactions as a part of the Journal of the American Chemical Society, or as a separate journal.

Prof. J. W. Richards: The tentative proposition made by the committee of the American Chemical Society is to the effect that a new journal be started, which shall be published by the two societies, and shall be the official organ of this Society. That new journal would include all the transactions of the American

Electrochemical Society, all the papers on physical and electrochemical subjects now published in the Journal of the American Chemical Society, and the contents of the Journal of Physical Chemistry. It would be published jointly by both societies, and be the organ of this Society.

The present status of the matter is that a committee has been appointed by each Society to confer upon it. The committee of the American Chemical Society has made a tentative proposition for discussion; there has been a consideration of this by the committee of this Society, and it is in process of drawing up a counter proposition which will embody its views. The matter has not formally gone before the Board of Directors of either Society for action, the idea being that it would not go before the Board of Directors of either Society until the two committees had unanimously agreed upon a plan they thought equitable and fair; in that case, it would be submitted to the boards of both Societies for their consideration, and it would be a question, then, as to whether the boards of the societies would endorse the proposition.

The present question which the Board of Directors of the American Electrochemical Society desires to have discussed is not so much as to which of the two methods which have been outlined for carrying out the details of the process are preferable, but as to the general proposition—would such a combination be desirable, if it could be practically arranged with fairness and equity to both sides? If answered affirmatively, this gives the two committees a backing that they have not possessed; it would give to the Board of Directors, also, the opinion of the Society—that if such an arrangement could be made with fairness to both, it should be made.

Before closing this discussion, I will ask the sense of the Meeting on the general question of the advisability of this combination, if the details can be arranged in a manner perfectly satisfactory to the governing bodies of both Societies.

Mr. Reed: It seems to me that no vote on the question ought to be taken at this time. I do not think that a vote would be representative, at any of these meetings. There is too small a percentage of the members present. No notice of it has been given to the other members, either. It seems to me a vote on a question of such importance as this should be taken by mail, so that we might get an expression from all the members of the Society, and it ought to be done after they have had a chance to consider it. A vote now would be premature.

PROF. C. F. BURGESS: I agree with Mr. Reed's views. I have given this matter some thought; I read the report yesterday, and I can see some very fundamental reasons why the scheme should not be entered into. I cannot present those reasons as well as I should like, because I have not had an opportunity to get the data together. I have the impression that 70 per cent. to 80 per cent. of our membership embraces men who are in industrial work, men who are interested in purely technical papers more than they are in scientific papers or pure science, and I am of the opinion that those members would be opposed to any absorption of this Society by another society, which is an extreme view of what would occur if we entered into this joint arrangement. It must be admitted that the dress in which this Society appears before the public is its published Transactions. If we call that publication by some other name—some name other than the Transactions of the American Electrochemical Society—we are sacrificing much of our individuality. As has been stated, only a small percentage of our membership attends the meetings. We draw the membership by offering certain inducements, and the inducement, the principal one, is that we give them the Transactions, and that is the inducement that would not attract if we withdrew it. I agree with Mr. Isakovics that the membership would fall off very rapidly. Then, also, members now members of both this and the American Chemical Society would simply transfer their allegiance to the American Chemical Society, and we would not have any good arguments for the drawing of new membership into this Society.

PRESIDENT HERING: I thoroughly agree with Mr. Reed that this is hardly the place to take a vote. I think it is a good place for members to express their views, but not a good time to take a vote. A vote should be by mail, as he says.

PROF. J. W. RICHARDS:. The chair will entertain a motion either way, either an immediate vote expressing the sense of the meeting, as advisory to the Board of Directors, or that a vote be taken by mail.

I think the Board of Directors would like to have the sense of the Meeting, either by expressing it by a present vote, or that the matter be put to a mail vote.

MR. SPERRY: I move that the sense of the Society be given in a mail vote, and that the members be furnished with full information on the matter, especially as to what our Transactions would be under the proposed arrangement, and how much they would represent us, and also comparing—if anyone can make it in the concrete—how many volumes we would have at our disposal under the proposed arrangement, and how that would fit in with our past experience on the sale of back volumes. (Motion seconded.)

PROF. J. W. RICHARDS: Mr. Sperry has moved, and it has been seconded, that the sense of the membership be taken by mail vote, as a guide to the Board of Directors in this matter. All in favor of so referring this question say aye; any opposed, nay. The motion is carried.

PROF. L. KAHLENBERG: *(Communicated)* With what Mr. Hering said in his address, I certainly agree in the main. The Society must maintain independence in the matter of the publication of its Transactions. I hope the day will never come when all chemical publications will have to be passed upon by one Publication Committee, no matter how able that committee may be or under what society it may operate. It will cost a little more to publish independently, but in the interests of the advancement of science we ought cheerfully to incur this additional expense. I hope that day will never come when a meritorius paper will have to be sent abroad to be published because an American committee practically controlling the matter of the publication of chemical articles has turned the paper down. Individual effort will ever be the basis of the highest progress in science, and the same is true of the individual efforts of the young, enthusiastic scientific societies organized to advance knowledge in some special fields. We must expect that in the future still other independent societies will spring up to cultivate special fields in which chemistry is the basis; nor will this operate to the detriment of the American Chemical Society, in whose work and whose welfare I have always maintained a deep interest. Just as the A. A. A. S. has been somewhat apprehensive of the development of various scientific societies, so now the American Chemical Society entertains similar feelings towards the development of societies organized to further biological—and electro—chemistry. We need not have fear that anything but good will spring from the formation of new societies for special purposes by hundreds of enthusiastic workers.

A paper read at the Eleventh General Meeting of the American Electrochemical Society, at Philadelphia, May 3, 1907, President Carl Hering in the chair.

THE ELECTROLYTIC CORROSION OF BRASSES.

By Azariah Thomas Lincoln.

(Research Award, 1906.)

The great importance of the subject of corrosion of metals has no doubt led to the granting of an award, by the American Electrochemical Society, for a research on the electrolytic corrosion of brass. Considerable interest in the corrosion of metals is being manifested along various lines at present. It is well known that fence wire, which is made of modern Bessemer and open hearth steel, does not last nearly so long as the wire made twenty or twenty-five years ago; iron and steel placed in concrete, when made the anode, are readily corroded by a small electric current; dissimilar metals placed together in sea water corrode badly. There are numerous other references to corrosion of metals and alloys, and to some cases where serious financial losses have just been averted by the timely discovery of badly corroded parts of large steamers and various other machinery used under water.

Corrosion is known to be electrolytic in many cases, and purely chemical in others. It is rather generally recognized that chemical and electrolytic corrosion are practically identical, and recently this has been clearly shown by Turrentine,[1] in the case of the action of nitric acid on copper. Hence, in the corrosion of alloys by means of the electric current, the amount of corrosion which it would take years to obtain chemically, can be obtained in a few hours electrochemically.

In carrying out this investigation on the electrolytic corrosion of brasses, the method used was in general that employed by Mr. Curry[2] in his research on the electrolytic corrosion of bronzes. Our work has been confined primarily to the corrosion of the pure copper-zinc alloys, but a few experiments were made

[1] Jour. Phys. Chem., *10*, 715 (1906).

[2] Jour. Phys. Chem., *10*, 474 (1906).

on the corrosion of copper-zinc-tin alloys containing a small percentage of tin. The constitution of alloys of copper and zinc has been a problem that has elicited the attention of a number of workers, but it was not until a few years ago that Shephard[3] showed conclusively that in the system copper-zinc there are no definite compounds. He confirmed the work of Roberts-Austin that the liquidus consists of six branches, which indicate that there are six solid solutions, one in equilibrium with each branch of the freezing point curve. The equilibrium curves, as worked out by Shephard, are represented diagrammatically in Fig. 1.

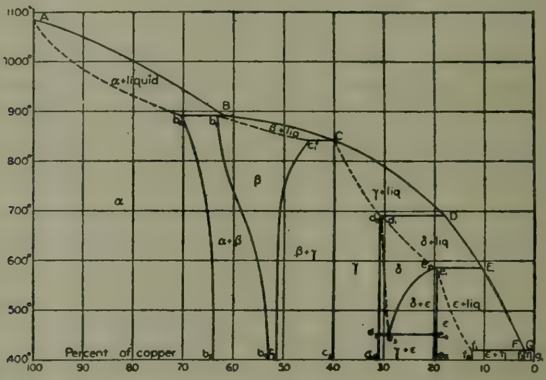

FIG. 1.

The compositions of the various solid solutions are represented, and the stable forms under various heat treatments. We shall only consider the solid solutions that constitute the alloys when they are annealed at 400° C., which temperature is represented by the lowest horizontal line in the figure. From pure copper to 64 per cent. copper, we have alloys of homogeneous α crystals; from 64 to 53.5 per cent. they consist of pure α crystals, scattered throughout the main mass of β, while from 53.5 to 51 per cent. we have a solid solution of pure β. From 51 to 40 per cent., γ crystals separate out from the β, and this sometimes results in forming large masses of the γ crystals, with a very marked decrease in the amount of β as the copper constant decreases.

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[3] Jour. Phys. Chem., *8*, 421 (1904).

From 40 to 31 per cent., copper, the alloy consists of homogeneous γ, and those containing from 31 to 20 per cent. will vary greatly in structure with the heat treatment. Those annealed below 450° C. consist of a mixture of γ and ϵ, the alloy being composed largely of the solid solution ϵ, which contains a few γ crystals, while between 20 and 12 per cent. we have practically pure ϵ solid solution. Below the freezing point of alloys, ranging in composition between 12 and 2.5 per cent. copper, the phase that separates out is the stable one, and the annealed and cast samples are similar homogeneous mixtures of ϵ and η crystals. From 2.5 per cent. copper to pure zinc, the annealed samples are homogeneous, and all similar in structure, consisting largely of η crystals.

Brasses were prepared representing all of these stable forms, at 400° C. (except the γ crystals), by melting pure electrolytic copper in a Battersea crucible under pulverized charcoal, to prevent oxidation. When the copper was melted, the requisite amount of zinc was added, in small quantities at a time, and stirred with a graphite rod after each addition. When the melt was supposed to be homogeneous and ready to pour, the charcoal was skimmed off, the melt stirred thoroughly with the graphite rod, and poured very quickly into a sand mould. Sand moulds were employed, as they were found much more satisfactory than moulds of graphite and iron, which were worked with for a long time without obtaining good sound castings. The pattern was made of a 7-inch brass rod, ½-inch in diameter, through which were drilled seven ¼-inch holes, and into these were inserted ¼-inch brass rods, 9 inches long, extending at equal distances on either side of the main rod. Great care was taken to have the center of all of these rods in the same plane. A plaster-of-Paris half-mould was made; upon this a sand half-mould was prepared, and then the other sand half-mould was made upon this. A ½-inch "gate" to the center of the form and two "risers," of about the same diameter near the ends of the central part, were provided. The mould was then further vented by perforating the sand by means of a small iron wire. The sand used was the ordinary sand employed for casting brass. With this form of sand mould, very perfect and acceptable castings were readily obtained. The castings were removed as soon as they were solid enough to handle, and cooled in water. Sometimes they were nearly red hot. The small ¼-inch lateral rods were then removed by a hack-saw. Two rods from different parts of the casting were filed and highly polished, and one piece was cut from the end of one, near the "gate," and from the free end of the other. These pieces were selected for analysis and half-gram portions were taken, and the copper determined electrolytically. From the numerous analyses made, there seemed to be no question but that the castings were of uniform composition, as the following data show:

No. of sample	Per cent. of copper	
	1	2
1	86.66	86.66
2	73.38	73.44
3	58.52	58.46
4	51.42	51.48

After having ascertained in this manner that the pieces from the castings were of the proper composition and would represent the desired phases, they were placed in a German silver resistance furnace, similar to the one described by Shephard, and annealed at 400° C. for two weeks. They were then allowed to cool in the furnace. These pieces were then turned down, by means of a 3/16-inch hollow tool, and cut off to the required length (3.5 inches), highly polished, numbered, and stored in glass-stoppered bottles, where they remained bright for months. The test pieces from some castings were too brittle to be worked, and those representing pure γ crystals were all used up in the attempt to machine them, and no others were prepared. The series prepared represented all the solid solutions stable at 400° C., with the exception of pure γ and η, and the test pieces employed in the corrosions had the following percentage composition of copper: 93.6, 86.6, 83.3, 76.3, 73.4, 66.5, 60.3, 56.8, 51.3, 47.6, 22.6, 10.5, 3.1.

The electrolytic corrosions were so arranged that the series of 13 test pieces could be corroded simultaneously in the same electrolyte. A wooden frame standing about 5 inches above the desk was arranged to carry, at a distance of 5 inches apart, 13 two-grooved wooden pulleys, each of which was attached to a 3/16-inch brass rod running in a brass sleeve. These rods were provided at the lower end with an ordinary double connector, by means of which the test piece was attached to the stirrer, while in the upper end of the rod was drilled a small hole, into which mercury was placed, to insure a good contact with the wire conducting the current to the test piece. The apparatus consisted of two sections, one carrying six, and the other seven, stirrers, and each set driven by its own motor, belted direct to one of the central pulleys, which was 2 inches in diameter. The other pulleys, 1 inch in diameter, were connected on either side of this one, in series, by a belt of round silk elastic, which was found very convenient for running pulleys, the distance between which is fixed. The fan motors used were of the same pattern and speed. Platinum wires were employed for the cathodes, and the current was conducted through the test pieces placed in series. Normal solutions were used, being approximately of the same strength Curry used in his work. Two hundred cubic centimeters of the electrolyte were used in each case. The experiments were conducted at room temperature, and usually lasted for about eight hours. No attempt was made to have a current of exactly the same amperage maintained, nor was the same current used in the various exercises. The test pieces were immersed to the depth of 2 inches (5 cm.), exposing a surface of 1.2 square inches (7.7 sq. cm.). This was practically constant in all of the determinations, and for all of the test pieces, except those which were used several times. In those cases, the surfaces were always filed and smoothed with emery cloth and then polished. The area of some of these would be slightly smaller than the new samples, but this slight change in the current density would make no material difference, as no attempt was made to employ exactly the same current in the corrosions in various liquids.

At the conclusion of the corrosion, each test piece was thoroughly cleaned, by the aid of a rubber-tipped stirring rod. It was not always an easy matter to clean the test pieces in this manner, as frequently there was found a test piece on which there remained a copper-colored coating, which could not be removed by scraping with a knife.

The precipitate resulting from the corrosion was dissolved in nitric acid, and the copper content of the corrosion product determined electrolytically. Cylindrical platinum gauze cathodes and a rotating spiral platinum anode were employed. This method, being practically the same as the one recently described by Perkins,[4] was in use by us for months before his description appeared. Most of the corrosion experiments were run in duplicate, and some of them more times. The results herein presented indicate simply the general trend of the corrosion of the brasses.

The following solutions were employed in the electrochemical tests: Sodium chloride, sodium nitrate, sodium sulphate, sodium acetate, sodium carbonate, sodium phosphate, ammonium nitrate, ammonium oxalate, acid ammonium oxalate.

In the experiments to test the chemical corrosion, the following solutions were used: Sodium chloride, sodium nitrate, sodium persulphate, and alkaline sodium persulphate. Air was bubbled through these solutions for several weeks.

As complex brasses are of great commercial importance, test pieces were prepared of copper-zinc-tin alloys, containing a small percentage of tin. These were subjected to electrolytic corrosion in the same manner as the simple brasses in solutions of sodium chloride, sodium nitrate, and sodium sulphate.

Corrosion in Sodium Chloride Solution.

The data are given in Table I for the electrolytic corrosion in a normal sodium chloride solution. In the first column is given the composition of the test pieces, expressed in percentage of copper; in the second column, the number of grams the test pieces lost during corrosion, *i. e.,* the weight of the corrosion produced; in the third column, the number of grams of copper in the corrosion produced; in the fourth column we have the percentage of copper in the corrosion product. In the last column is given the so-called current efficiency.

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[4] Trans. Faraday Soc., *2*, 91 (1907).

TABLE I.

Percentage of copper in test pieces	Grams of corrosion	Grams of copper in corrosion	Percentage of copper in corrosion	Current efficiency
93.6	.7204	.6756	93.8	100.5
86.6	.7165	.6263	87.4	103.7
83.2	.6935	.5807	83.7	102.0
76.3	.6519	.4993	76.6	99.5
73.4	.6460	.5117	79.2	100.6
66.5	.6056	.4026	66.5	97.5
60.3	.5773	.3417	59.2	96.2
56.8	.4576	.1150	25.1	77.6
51.3	.4618	.0990	21.4	80.5
47.6	.4077	.0052	1.3	72.8
22.6	.4042	.0006	0.2	86.0
10.5	.3975	.0004	0.1	92.7
3.1	.3972	.0001	0.0	98.3

After the corrosion has been running for a few minutes in the sodium chloride, a light green, flocculent precipitate appears which soon changes to a dark yellow or orange color. This is present in all cases except the three lower brasses, where the precipitate remains almost pure white. No other electrolyte gives the same colored corrosion product. At the termination of the corrosion, the test pieces were found to be coated with a heavy red scale, in most cases easily removable, while in one or two cases not even scraping was efficacious. In observing the 51.3 per cent. brass a few days after running a corrosion test, it was noticed that the scale had become loosened and could be readily peeled off. This scale was removed, weighed, and analyzed, with the result that 0.3172 grams of the scale gave 0.3140 grams of copper, thus showing that the scale was about 99 per cent. pure copper.

The copper in the corrosion product was obtained by first depositing the copper from an ammoniacal solution, dissolving in nitric acid and redepositing.

In Fig. 2 is represented diagrammatically the relation between the number of grams of the corrosion product and the composition of the brass. The boundaries of the different solid solutions are represented by the vertical dotted lines, and the areas are designated by the kind of stable crystals present. The percentages of copper are represented by the abscissas, and the ordinates represent grams. The upper curve shows the variations in the amounts of corrosion with the change in concentration. There are no data for the γ field, and the immediate regions of adjoining areas, so the values represented by this portion of the curve are interpolated. There is a rapid decrease in the amount of corrosion with the decrease in the copper content extending across the areas for α, α + β and β crystals, when it drops very quickly in the β + γ area to nearly 50 per cent. of the corrosion in the brasses of highest copper content. From

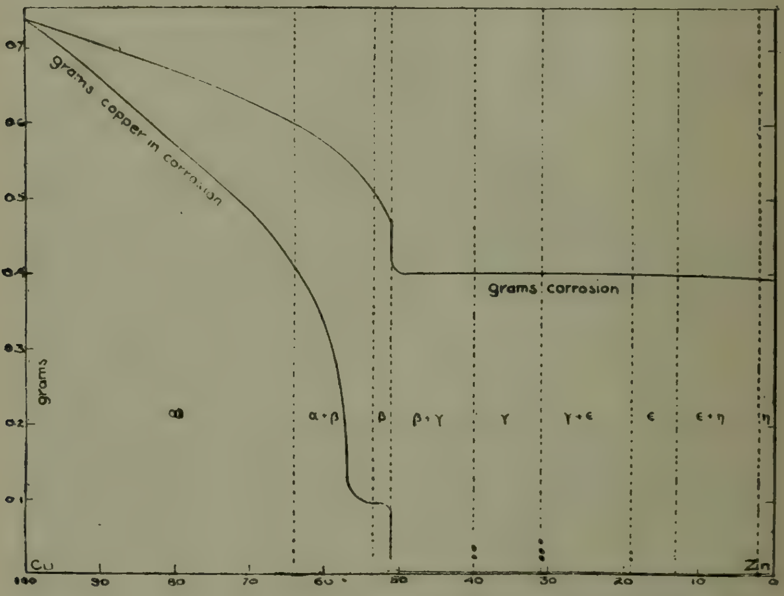

FIG. 2.

about 50 per cent. brass to pure zinc the amount of corrosion remains practically constant, the different crystalline forms, γ, ε and η, do not seem to affect the amount of corrosion. The lower curve represents the grams of copper in the corrosion product, from which it is apparent that the amount of copper decreases very rapidly with the decrease in the copper content of the test piece, becoming practically zero for 50 per cent. brass, and remaining that for all other brasses between this and pure zinc. The fact that practically no copper dissolves from brasses containing less than 60 per cent. copper, leaves the surface of those copper-rich. This explains why the coating from the 51.3 per cent. brass, mentioned above, was 99 per cent. copper.

The apparent current efficiency, represented in the last column of Table I, was calculated upon the basis of the electrochemical equivalents of pure copper and pure zinc, the copper dissolving as cuprous chloride. The corrosion of brass of any intermediate composition we assume would be equal to the sum of the copper and zinc corrosion of the same composition. It is perfectly apparent that such a state of affairs need not necessarily exist, for the copper and zinc may exist in brass in such a form as to yield a product much more readily corroded than pure copper and pure zinc. If this occurred, it would account for current efficiencies greater than 100 per cent. The values given in the tables were obtained from the smoothed curves.

The brasses were examined microscopically after the corrosions, with very interesting and surprising results. Any description of the appearance of the corroded test pieces would give an inadequate idea of their appearance. There seems to be a definite relation between the appearance of the test piece after corrosion and the crystalline phases in equilibrium. A number of photographs were taken of various test pieces which had been corroded in the different solutions, and those represented in Figs. 13 to 18, inclusive, illustrate the characteristic appearance of the corrosion of α, $\alpha + \beta$, $\beta + \gamma$ and $\epsilon + \eta$ crystals. The Figs. 14 and 15 represent 76.3 per cent. and 56.8 per cent. brass, respectively, corroded in sodium chloride solutions. They are somewhat magnified (x 14), in order to bring out the structure, and, owing to the small diameter of the test pieces, difficulties were encountered in getting larger areas in focus at one time.

Corrosion in Sodium Nitrate Solution.

The data obtained from the results of the corrosion in normal sodium nitrate solutions are given in Table II. The headings of the columns have the same significance in this table as in Table I and the subsequent tables, and are self-explanatory. The data from two series of experiments are incorporated under "A" and "B."

TABLE II.

Series	Percentage of copper in test piece	Grams of corrosion	Grams of copper in corrosion	Percentage of copper in corrosion	Current Efficency
A	93.6	.2617	.2410	92.1	
	86.6	.2591	.2240	86.5	
	83.3	.2773	.2236	82.5	
	76.3	.2746	.2024	73.7	
	73.4	.2782	.2044	73.5	
	66.5	.2618	.1562	60.0	
	60 3	.2960	.1776	60 0	
	56.8	.2774	.1500	54.1	
	51.3	.2786	.1494	53.6	
	47.6	.2855	.1018	35.7	
	22.6	.2111	.0000	00.0	
	10.5	.2717	.0125	4.6	
	3.1	.3916	.0116	3.0	
B	93.6	.3091	.2877	95.2	103.0
	86.6	.3191	.2775	86.9	106.6
	83.3	.3173	.2645	83 4	108.3
	76.3	.3308	.2494	75.4	111.0
	73.4	.3375	.2481	75.2	111.6
	66.5	.3398	.2238	65 8	112.4
	60.3	.3452	.2105	61.0	113.1
	56.8	.3355	.1872	55.8	109.8
	51.3	.3375	.1812	53.7	111.4
	47.6	.3504	.1516	43.2	114.7
	22 6	.2352	.0002	00.0	75 8
	10.5	.3316	.0228	6.8	106.1
	3.1	.4804	.0174	3.6	154.0

In sodium nitrate solution the corrosion products were apparently hydroxides of copper and of zinc, in varying proportions. The corrosion product from the 3.1 per cent. brass was gray colored, due to metallic particles mixed with the zinc hydroxide. The test pieces were coated with a red scale, easily removable, and exposing the bright surface of the brass underneath on which was a beautifully-marked crystalline structure.

Fig. 3 represents, diagrammatically, as in Fig. 2 and the subsequent figures, the relation of the grams of corrosion, the grams of copper in the corrosion product, and the variation of these with the change in composition of the brass, while the vertical dotted lines represent the boundaries of the different solid solutions. The upper curve represents a gradual increase in the amount of the corrosion product with the decrease in the copper content of the brass, until the $\beta + \gamma$ area is reached. While in the $\gamma + \epsilon$ area the 22.6 per cent. brass shows very much less corrosion, while with the further decrease in the copper content there is a very marked increase in the amount of corrosion. A prolongation of this curve to the zinc axis would indicate the great corrosion of pure zinc, being about twice that for pure copper. Pieces of pure copper and pure zinc were corroded in normal sodium nitrate solution in series with a copper coulometer, with the following results:

	1	2	
Copper..........	0.3922	0.3719	grams corrosion
Zinc	0.3656	0.3763	" "
Coulometer	0.3719	0.3497	" deposition

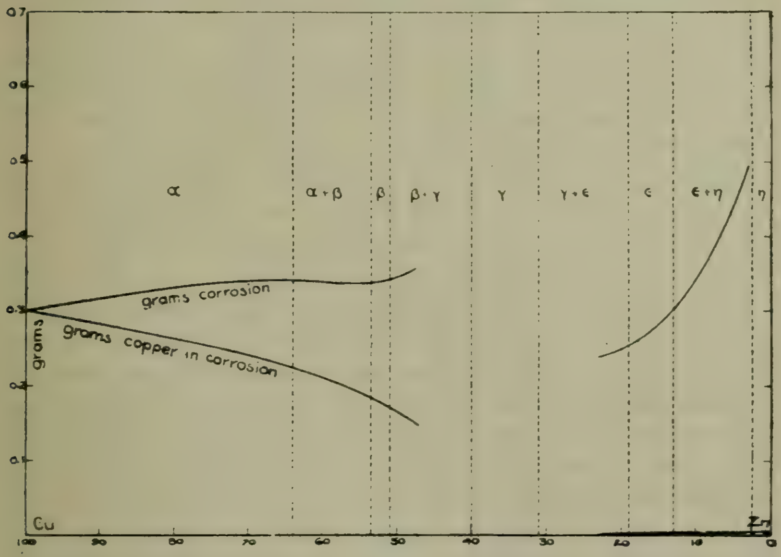

FIG. 3.

From these data it appears that practically the same amounts of copper and zinc are corroded from anodes of the pure metals, and the current efficiency given in the last column of Table II was calculated upon this basis. The large amount of corrosion obtained in the brasses low in copper is undoubtedly due to several factors, which are no doubt similar to those Mr. Curry had to deal with in the corrosion of bronzes in sodium nitrate solution. He showed that some of the crystals were dislodged by the matrix being dissolved away, and these dropped from the test piece and remained undissolved in the nitrate solution. The high corrosion of the low copper bronzes he then attributed to disintegration, which no doubt accounts for the high corrosion in the case of the low copper brasses.

From the lower curve in Fig. 3 we observe the relation of the amount of copper in the corrosion product and the test piece. From a comparison of the last column in Table II and the second column, it is apparent that the corrosion product is of the same composition as the test piece, until the γ phase appears in the brasses, when there is a marked difference. The amount of copper in the corrosion products from the brasses consisting of $\gamma + \epsilon$ crystals is very small. For brasses of less copper content the amount of copper in the corrosion product increases at first, and then decreases. The composition of the corrosion product from the brasses, containing only a few per cent. of copper (the ϵ and η crystals), is virtually the same as the test piece.

The test pieces in sodium nitrate solution become coated with an easily-removable scale, and this was true of the pure copper in the experiment referred to above. When these scales are removed, a bright metallic surface is exposed. An effort was made to ascertain if any relation existed between the corrosion and this scale. A number of test pieces were corroded, as usual, in the normal nitrate solution, and an attempt was made to separate the scale, which was formed, from the remainder of the corrosion product by dissolving the hydroxides in dilute sulphuric acid, and immediately filtering the scale upon previously weighed filter papers. The filter papers and scale were dried and weighed, and then the copper in the scale determined. In Table III these data are presented. In column one is given the percentage of copper in the test piece; the grams of corrosion in the second; the total corrosion less the weight of the scale in the third; in the fourth, the weight of copper in the corrosion product; in the fifth, the weight of copper in the corrosion product, less the weight of copper in the scale; the sixth, the percentage of copper in the corrosion product; while in the last column we have the percentage, the copper in the corrosion product, less the scale, is of the total corrosion, *i. e.*, the percentage the fifth column is of the second.

TABLE III.

Percentage of copper in test piece	Grams of corrosion	Grams of corrosion less grams of scale	Grams of copper in total corrosion	Grams of copper in total corrosion less grams of copper in scale	Percentage of copper in total corrosion	Percentage copper in residue is of total corrosion
93.6	.3479	.2848				
86.6	.3538	.3371	.2964	.2952	86.6	86.1
83.2	.3428	.3379	.2943	.2888	83.1	81.6
76.3	.3596	.3355	.2690	.2542	74.8	70.1
73.4	.3616	.3212	.2671	.2414	73.9	66.8
66.5	.3549	.3092	.2290	.2110	64.5	59.5
60.3	.3621	.3386	.2157	.2081	59.6	57.5
56.8	.3616	.3494	.2038	.1973	56.3	54.6
51.3	.3750	.3289	.1987	.1650	53.0	44.0
47.6	.3866	.3327	.1840	.1512	47.6	39.1
22.6	.2697	.2565				
10.5	.3649	.3297	.0258	.0163	7.1	4.5
3.1	.5520	.4052	.0202	.0044	3.7	0.8

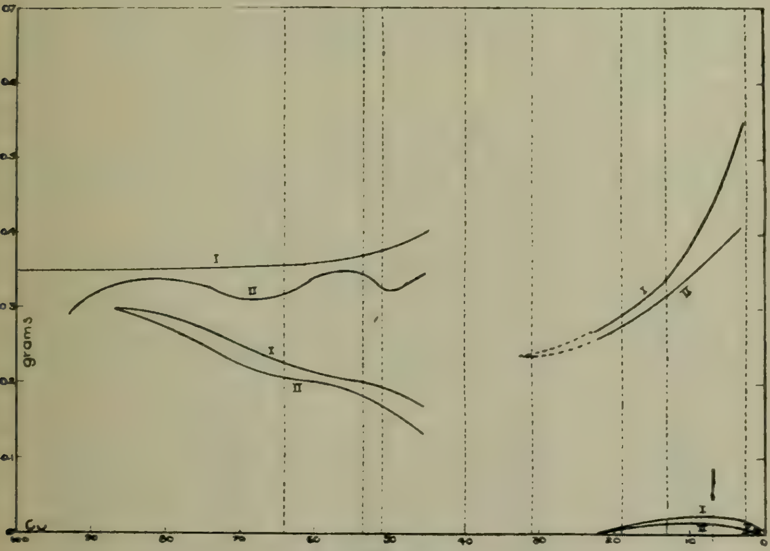

FIG. 4.

From the data herein presented, and also from the representation in Fig. 4, no apparent relation exists between the grams of corrosion and grams of scale, which are designated "I" and "II," respectively, by the upper curves. The lower curves "I" and "II" represent the grams of copper in the corrosion product, and the grams of copper in this after the amount in the scale has been deducted. These may indicate in a general way that for brasses containing chiefly γ crystals or $\gamma + \epsilon$ crystals there may be no scale formation on the test pieces.

Figures 16 and 17, representing the photographs of corroded surfaces of 47.6 per cent. brass and 3.1 per cent. brass, respectively, in sodium nitrate solutions, indicate very clearly the uneven corrosion of the surfaces and the marked way in which the crystals are dissolved out (Fig. 17), and the very deep pitting of the brasses of low copper content. Where such marked holes are produced, there is not much doubt but that certain crystals are really loosened by having the material dissolved from around them, and being more resistant to the solvent action, may become dislodged, and drop from the test piece into the solution, there eventually to be considered a part of the corrosion product. Curry[5] has shown in his work on the bronzes that there are many such cases, wherein the so-called corrosion product is the result of this disintegration and of the dissolving action of the electric current as well.

Corrosion in Sodium Sulphate Solution.

The data obtained from the results of the corrosion in normal sodium sulphate solutions are given in Table IV.

TABLE IV.

Percentage of copper in test piece	Grams of corrosion	Grams of copper in corrosion	Percentage of copper in corrosion	Current efficiency
93.6	.1184	.1069	90.3	100.0
86.6	.1184	.1012	85.5	100.0
83.3	.1177	.0888	75.5	100.0
76.3	.1192	.0907	76.1	100.0
73.4	.1188	.0845	71.2	100.0
66.5	.1192	.0756	63.4	100.0
60.3	.1214	.0688	56.7	100.0
56.8	.1172	.0515	44.0	100.0
51.3	.1136	.0357	31.4	100.0
47.6	.1132	.0015	1.33	100.0
22.6	.1031	.0010	0.97	89.7
10.5	.1094	.0003	0.28	95.1
3.1	.1116	.0002	0.18	97.0

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[5] *Loc. cit.*

The test pieces were coated with a red scale, and the general character of the corrosion products was the same as in the sodium nitrate solution.

The amount of corrosion is practically the same for all of the brasses, and this is clearly shown by the upper curve in Fig. 5. From a comparison of the first and last columns in Table IV, it is readily seen that the brasses containing less than about 70 per cent. become copper-rich on the surface. As shown by the lower curve in Fig. 5, the appearance of the γ crystals again affects the amount of copper in the corrosion product. Brasses below 47.6 per cent. copper contain practically no copper in the corrosion product.

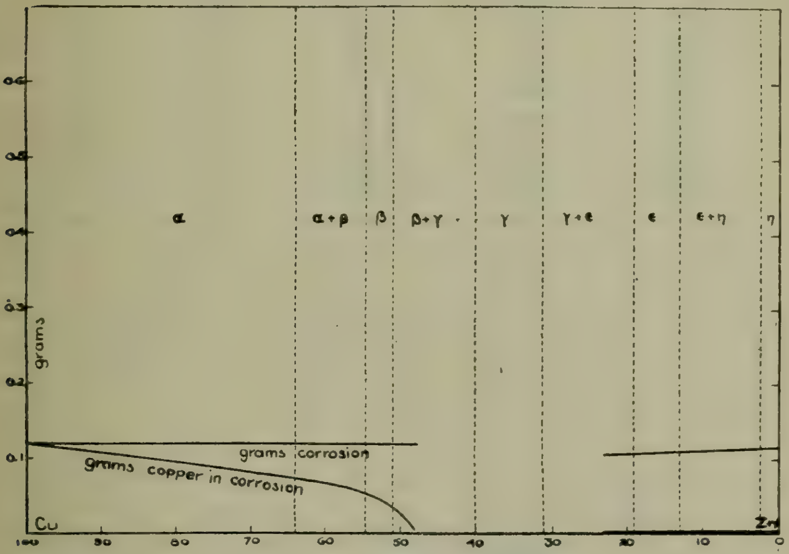

FIG. 5.

The set of test pieces used in the sodium sulphate solution were reduced in a current of hydrogen, in order to ascertain the amount of oxide present, and also to determine whether there was present an invisible film on those test pieces that remained bright. The loss was insignificant. The test pieces used in the other solutions which showed any indication of the oxide being present were reduced, and the proper corrections made.

Corrosion in Sodium Acetate Solution.

The data for the electrolytic corrosion in normal sodium acetate solutions are given in Table V.

TABLE V.

Percentage of copper in test piece	Grams of corrosion	Grams of copper in corrosion	Percentage of copper in corrosion	Current efficiency
93.6	.1107	.1036	93.6	46.0
86.6	.2656	.2311	87.0	90.8
83.2	.2623	.2139	81.5	103.0
76.3	.3710	.2785	75.1	116.6
73.4	.3661	.2719	74.3	119.3
66.5	.4021	.2668	66.3	121.7
60.3	.4094	.2397	58.5	118.1
56.8	.4120	.2247	54.5	118.1
51.3	.4397	.2249	51.1	114.7
47.6	.4318	.2043	47.3	113.0
22.6	.3254	.0015	0.0	71.8
10.5	.3458	.0022	0.0	70.0
3.1	.4483	.0147	3.3	86.5

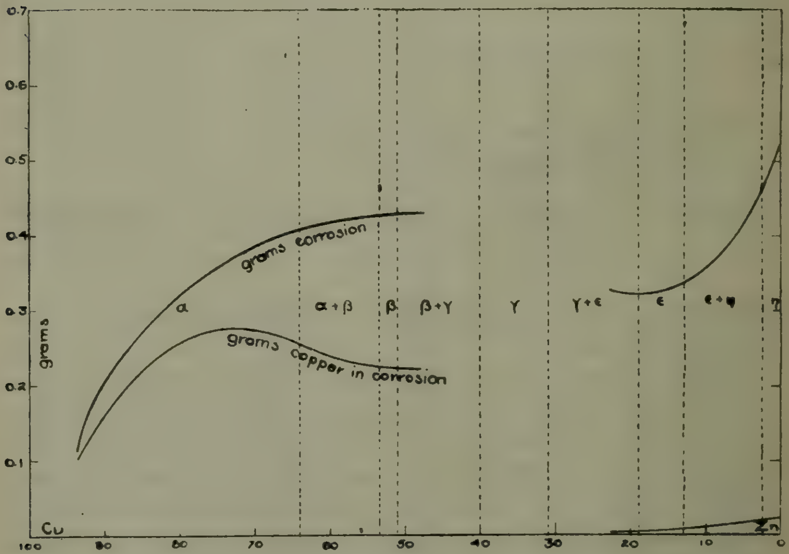

FIG. 6.

From the second column it is apparent that the amount of corrosion increases very rapidly with the decrease in the copper content.

This is clearly seen from the upper curve in Fig. 6, the maximum value being reached with the appearance of the γ crystals; then, from interpolation, the corrosion apparently decreases rapidly to about 22.6 per cent. brass, beyond which the amount of corrosion increases very rapidly. The values for the amount of corrosion of brasses of high copper were not obtained by exterpolation, because the exact nature of the curve is not known, but it undoubtedly ascends very rapidly, and cuts the ordinate at about 0.23 grams, as is shown by the following experiment.

A piece of pure copper in a normal sodium acetate solution was placed in series with a copper voltameter. The copper lost 0.1565 grams, while the voltameter registered a gain of 0.3719 grams, and 0.1491 grams against 0.3497 grams in the voltameter. The copper electrode remained perfectly clean and bright, as did the 93.6 per cent. brass electrode. There was not the slightest trace of a scale. In the case of the brasses of high copper content, the corrosion product has practically the same composition as the test piece, while for the test pieces which are least corroded the corrosion product was virtually pure zinc. We have here again the marked influence of the γ crystals on the corrosion.

In calculating the current efficiency, the grams of pure copper corrosion were interpolated from a later experiment on the corrosion of pure copper in sodium acetate solution. The grams of zinc corrosion were obtained from exterpolation of the curve.

Corrosion in Sodium Carbonate Solution.

The data, as recorded in Table VI, represent the results of a determination of the corrosion of the test pieces in normal sodium carbonate solutions.

It is apparent that there was but very little corrosion. There was experienced great difficulty in getting any current through the test pieces, due to the formation of insulating films. This was particularly true in the case of the 10.5 per cent. and 3.1

Table VI.

Percentage of copper in test piece	Grams of corrosion	Percentage of copper in test piece	Grams of corrosion
93.6	.0022	51.3	.0066
86.6	.0015	47.6	.0158
83.3	.0019	22.6	.0191
76.3	.0040	10.5	.0032
66.5	.0018	3.1	.0149
60.3	.0022		.0095
56.8	.0046		

per cent. brasses, where a white adherent coating was formed. These test pieces were scraped off, washed free from the sodium carbonate solution, and when tested with an acid solution, gave a strong test for carbonates. These cleaned test pieces were replaced in the series, and the current went up rapidly to 0.15 ampere, but immediately dropped to almost nothing. At the end of the test, the 51.3 per cent. and 47.6 per cent. brasses were covered with a green film, while the other test pieces were only slightly discolored.

Corrosion in Ammonium Nitrate Solution.

The data for the results of electrolytic corrosion in normal ammonium nitrate solution are given in Table VII.

Table VII.

Percentage of copper in test piece	Grams of corrosion	Grams of copper in corrosion	Percentage of copper in corrosion	Current efficiency
93.6	.3976	.3723	93.6	100.0
86.6	.4032	.3461	84.8	100.0
83.2	.4158	.3459	83.2	100.0
76.3	.4162	.3121	75.0	100.0
73.4	.4306	.3152	73.2	100.6
66.5	.4332	.2852	65.8	102.5
60.3	.4202	.2511	59.7	105.5
56.8	.4471	.2516	56.3	107.3
51.3	.4424	.2378	53.7	114.7
47.6	.5014	.2242	44.7	122.0
22.6	.3908	.0302	7.7	94.0
10.5	.4707	.0341	7.2	113.3
3.1	.6582	.0231	3.5	135.0

The corrosion is very similar to what takes place in the sodium nitrate solutions. The amount of corrosion remains practically constant for the brasses representing the α crystals; it increases quite rapidly with further decrease in the copper content, showing that the β and γ crystals are more soluble than the α crystals. With the appearance of the ε crystals in the 22.6 per cent. brass, there is apparently a return to the normal corrosion as represented in the case of the α crystals. With further decrease in the copper content, the amount of corrosion increases very rapidly.

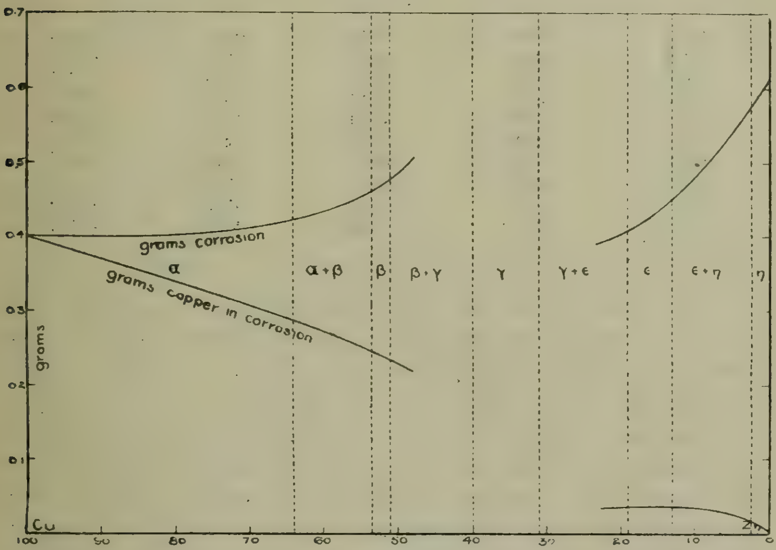

FIG. 7.

This is graphically represented in Fig. 7. The copper content of the corrosion product is practically the same as that of the test piece, with the exception of some of the brasses containing the ε crystals. The change in the cation of the electrolyte does not seem to affect the corrosion, since the general character is the same in both the sodium and ammonium nitrate solutions.

A representation of the appearance of the surface of a test piece containing 93.6 percentage of copper corroded in a normal ammonium nitrate solution, is given in Fig. 13. This is the typical appearance of the corroded surface of the brasses of high copper content.

Corrosion in Ammonium Oxalate Solution.

The data for electrolytic corrosion in normal ammonium oxalate solutions are given in Table VIII.

TABLE VIII.

Percentage of copper in test piece	Grams of corrosion	Grams of copper in corrosion	Percentage of copper in corrosion	Current efficiency
93.6	.4399	.4095	93.1	103.3
86.6	.4321	.3712	85.9	101.2
83.2	.4422	.3624	81.9	103.3
76.3	.4677	.3542	75.7	108.7
73.4	.4726	.3459	73.2	109.9
66.5	.4958	.3219	64.9	115.0
60.3	.4753	.2818	59.3	109.8
56.8	.5481	.3114	56.8	126.0
51.3	.4919	.2447	49.7	112.8
47.6	.4416	.2139	48.4	101.5

In the first experiments with this solution, all of the test pieces were employed, and the current decreased to practically zero, even when a pressure of 110 volts was employed. This is attributed to the fact that the test pieces low in copper developed insulating films, which did not break down even under high voltages. By the removal of the test pieces below 47.6 per cent. copper, the corrosion proceeded as in the other cases. The amount of corrosion increased with the decrease of the copper content, making a maximum in the brasses containing $\alpha + \beta$ crystals, and then decreasing very rapidly with the appearance of the γ crystals in the brasses of lower copper content.

This is shown graphically in Fig. 8, and again indicates the marked effect of the presence of γ crystals on the amount of corrosion. The copper in the corrosion produced does not vary much from that in the test piece, the curve representing the grams of copper in the corrosion product shows a gradual decreasing amount of copper with the decrease in the copper of the test piece.

Many efforts were made to determine the electrolytic corrosion of these brasses in a solution containing 3 per cent. ammonium oxalate and 3 per cent. oxalic acid. The results were very discordant, and a detailed discussion of the corrosion in this solution will be deferred until more data have been obtained. As the corrosion continued, the current decreased very rapidly, so that in a few minutes only a few milli-amperes of current were flowing. Increasing the pressure to 110 volts produced only temporary increase in the current, and it soon decreased to its lower value. In order to ascertain where the drop in potential occurred, a few measurements were made. The drop at the 47.6 per cent. brass was found to be 40 volts, while at the 51.3 per cent. brass it was 20 volts. It is, therefore, evident that excellent insulating films were developed, which even under very high impressed voltages would not break down.

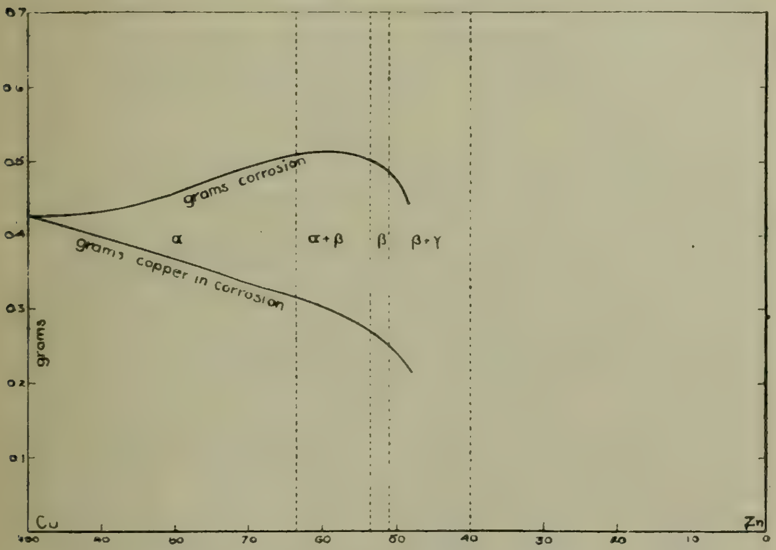

FIG. 8.

The same condition of affairs was found to prevail in the corrosion of the brasses in a normal solution of the tertiary sodium orthophosphate. A number of series of corrosions were run with this solution as the electrolyte, but the current decreased very rapidly, and the results obtained from the various series were not concordant. The cause of the rapid decrease was due to the formation of the insulating films on the test pieces, as is shown from the fact that the potential drop at the 10.5 per cent. brass was 60 volts, and the high pressure of 110 volts increased the current very little, and then only temporarily. These are practically the same conditions that were found in the case of the corrosions in the solution of normal sodium carbonate. It will be necessary to redetermine the corrosions in all three of these solutions, and collect the data very carefully, in order to ascertain fully the nature of the corrosions.

By representing his data diagrammatically, Mr. Curry[6] showed that the relation between the composition of the bronzes and the current efficiency brought out clearly the marked effect due to the phases of equilibrium. According to this idea, then, theoretically the brasses of intermediate composition should corrode in the proportion of their constituents. In the case of some bronzes of low copper content, Mr. Curry emphasizes the fact that in solutions of sodium nitrate the ϵ crystals do not dissolve, but become loosened by the matrix around them dissolving, and eventually dropping into the solution, where they become a part of the corrosion product. He attributes the fact that the current efficiency is over 100 per cent. to the presence of these disintegrated parts of the electrode in the corrosion product. He does not, however, emphasize the fact that in the bronzes of high copper content the copper corrosion is in excess of the theoretical amount, but he does indicate it in the diagram illustrating the current efficiency in acidified ammonium oxalate solution. In attempting to represent the current efficiency of the corrosion of brasses, we were likewise confronted with the current efficiency of over 100 per cent. in the high per cent. copper brasses in solutions of sodium nitrate, ammonium nitrate, and ammonium oxalate, as well as in those low in copper. These high current efficiencies in the low copper brasses could be attributed to disintegration. In view of the fact that there are, no doubt, several factors entering into the production of the corrosion product, and that at present we have no means of differentiating these, it would be fruitless to attempt to represent the current efficiency. We have, therefore, not presented any current efficiency diagrams, but used other methods for showing

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[6] *Loc. cit.*

the relation of the amount of corrosion and the phases in equilibrium, as well as the crystals that are readily corroded.

For ready comparison, the relation between the percentage of copper in the corrosion products and in the test pieces is represented diagrammatically in Fig. 9.

Curves are given for those six solvents in which the corrosion was found to be greatest. The abscissas represent the percentage of copper in the test pieces, and the ordinates the percentage of copper in the corrosion product. The similarity of the six curves is very marked. They show in general that the brasses of high copper content from about 47.6 per cent. up yield corrosion products of the same composition as the test pieces.

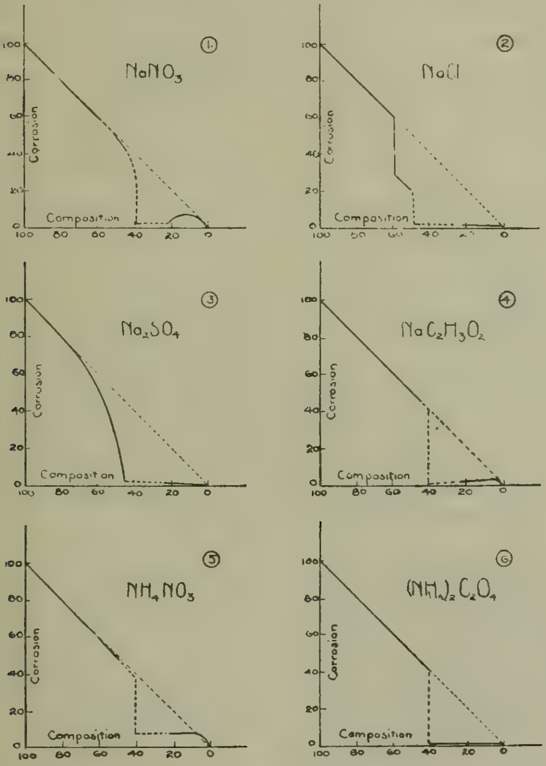

FIG. 9.

Those below about 20 per cent. copper become copper-rich on the surface, and the corrosion product is nearly pure zinc, while the interpolated values for brasses between 47.6 percentage and 22.6 percentage copper indicate practically a pure zinc corrosion product, which would mean a copper-rich surface. In the case of the corrosion product from sodium and ammonium nitrate solutions, curves 1 and 5, there is found a percentage of copper in the low copper brasses practically the same as in the test pieces, but this may be accounted for, owing to the deep pitting and great corrosion by the disintegration of the test piece, as indicated above. In the case of the corrosion in sodium chloride solutions (Curve 2), there is a very rapid decrease in the percentage of copper corrosion of brasses whose copper content varies between about 60 and 50 per cent. of copper. These brasses become copper rich on the surface, and the corrosion product is virtually pure zinc. These brasses represent closely the composition of Muntz's metal, and it is well known that Muntz's metal corrodes in sea water. The corrosion product obtained from sodium sulphate solutions (Curve 3) has the same composition as the test piece for brasses of 70 per cent. copper up, while for brasses below this the percentage of copper decreases very rapidly, reaching practically zero per cent. copper for 47.6 per cent. brass and for all brasses to pure zinc. Or, stating it differently, the brasses consisting of α, $\alpha + \beta$, or pure β solid solution, yield corrosion products in the six solutions named in Fig. 9, of practically the same percentage composition as the test pieces. The presence of γ crystals decreases the percentage of copper in the corrosion product enormously, and the brasses consisting of γ, $\beta + \gamma$, $\gamma + \epsilon$, or $\epsilon + \eta$ crystals yield corrosion products which are virtually pure zinc.

Chemical Corrosion of Brasses.

As it is generally held that chemical and electrochemical corrosion are identical, the same results should be obtained by both methods of corrosion. In order to ascertain this, the test pieces were allowed to stand in the solutions, and air bubbled through for several weeks. The solutions used were normal solutions of sodium chloride, sodium nitrate, sodium persulphate, and sodium persulphate containing 5 per cent. excess of sodium hydroxide.

The data from the results of the chemical corrosion in a normal sodium chloride solution are given in Table IX.

TABLE IX.

Percentage of copper in test piece	Grams of corrosion	Grams of copper in corrosion	Percentage of copper in corrosion
93.6	0.0866	0.0713	82.2
86.6	0.0692	0.0565	81.6
83.2	0.0571	0.0456	79.9
76.3	0.0168	0.0126	75.0
73.4	0.0131	0.0095	72.5

The test pieces in the sodium chloride solution became coated with a light green deposit, which was readily soluble in nitric acid without effervescence. From the table, it is readily seen that the amount of corrosion product decreases with the decrease in the copper content of the test piece, as occurred in the case of the electrical corrosion. A comparison of the last and first columns shows that the corrosion product contained less copper than the test piece.

In the sodium nitrate solutions, the test pieces showed practically no corrosion.

The chemical corrosion in the alkaline persulphate solution was very unsatisfactory. In most cases, the entire test piece was not immersed in the solution, but a part was exposed to the air. In these cases, there was a very marked difference in the corrosion of the immersed part and that exposed to the air, it being slight on the former, and extremely deep on the part in the air, and therefore the experiment was discontinued. Two days after the experiment was started, the solutions containing brasses of less than 51.3 per cent. copper became perceptibly blue. Before discarding the brasses, they were examined carefully, and the 93.6, 83.2 and 73.4 per cent. brasses were found to be badly corroded on the part of the test piece exposed to the air. The 22.6 per cent. brass, a silvery-white alloy, was entirely coated with a bright layer of copper. The 10.5 and 3.1 per cent. brasses were coated with a black deposit apparently crystalline in character. The 60.3 and 76.3 per cent. brasses remained practically unchanged.

The chemical corrosion in the persulphate solution did not yield any more gratifying results than those obtained in the alkaline persulphate solution. Before the experiment was discontinued, the test pieces were carefully examined, and the brasses of high copper content were found to be very badly corroded. The 51.3 per cent. brass was coated with a layer of copper, while the portion of the test piece exposed to the air was scarcely affected. The 3.1 per cent. brass was coated with a very rough layer of copper. The solutions containing the brasses of low copper content remained practically colorless, in contrast to those of the alkaline persulphate solution which were colored blue. Much more experimental data on the chemical corrosion of brasses will have to be obtained before a satisfactory comparison can be made between chemical and electrochemical corrosion.

Electrolytic Corrosion of Copper-Zinc-Tin Brasses.

Most of the commercial brasses contain, besides copper and zinc, small quantities of one or more other metals. The use of tin as the third metal is very common, and the substitution of a small quantity of it for zinc affects the physical properties of the brass very much, by increasing its hardness, strength, rigidity, and elasticity. Thurston[7] has investigated the physical properties of these copper-zinc-tin alloys, which he termed "kalchoids," and has shown that those containing about equal quantities of copper (58-54 per cent.) and zinc (40-44 per cent.) and small quantities of tin (0.5-2.5 per cent.) are the strongest "kalchoids." Guillet[8] has recently investigated a few copper-zinc-tin alloys micrographically, and states that "the introduction of tin has been shown by numerous experimenters to greatly increase the resistance to corrosion in sea water."

In the study of the electrochemical corrosion of the "kalchoids," it was our intention to prepare a number of castings, the composition of which would cover the whole range of concentrations representing the best and most valuable kalchoids. Only two series of castings were prepared, and it was found that these did not extend over sufficient range of copper content to include those described by Thurston. Nevertheless,

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[7] Thurston, Alloys, Brasses and Bronzes, Materials of Engineering, part 3.

[8] Revue de Metallurgie, Feb., 1905; Iron and Steel Mag., *10*, 21, 1905.

these were employed in some corrosion tests. No more castings could be obtained in the time at our disposal. The following table gives the composition of the two series of test pieces.

TABLE X.

SERIES I		SERIES II	
Percentage of copper	Percentage of tin	Percentage of copper	Percentage of tin
81.0	0.78	86.9	.98
77.1	0.78	77.2	.94
73.3	0.76	74.8	.90
64.0	0.77	71.4	1.02
58.9	0.79	66.7	1.07
54.8	0.75	63.0	1.05
54.7	0.65		

These brasses were prepared in a manner similar to that used in the preparation of the simple forms. The copper being first melted, the zinc and tin were then added, the melt thoroughly stirred, and then poured into the sand moulds. All test pieces were annealed at 400° C., and then turned down to uniform size by the 3/16-inch hollow tool. The tin in the test pieces was determined as stannic oxide by the ignition of the sulphide, as described by Olsen.[9]

The copper was determined electrolytically in the filtrates from the tin determinations. Usually, 3 or 4 grams of the test piece were employed for analysis, and duplicates taken. The amount of tin in the corrosion products was so very small that the data given in the tabulated results below must be considered merely as approximations, as much difficulty is experienced with the present methods in accurately determining small quantities of tin in presence of large quantities of copper and zinc.

Corrosion in Sodium Chloride Solution.

The data from the determination of the electrolytic corrosion of these sets of test pieces in a normal sodium chloride solution are given in Table XI.

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[9] Olsen, Quantitative Analysis, p. 142.

TABLE XI.

Percentage of copper in test piece	Percentage of tin in test piece	Gram s of corrosion	Grams of copper in corrosion	Grams of tin in corrosion	Percentage of copper in corrosion	Percentage of tin in corrosion
86.9	0.98	.8462	.7324	.0042	86.6	0.49
77.2	0.94	.7808	.6029	.0061	77.2	0.78
74.8	0.90	.7464	.5519		73.9	
71.4	1.02	.7597	.5445	.0072	71.7	1.03
66.7	1.07	.7545	.5067	.0078	67.3	0.49
63.0	1.05	.7529	.4751	.0037	63.1	0.93
81.0	0.78	.7895	.6405	.0073	81.1	0.52
77.1	0.78	.7808		.0040		
73.3	0.76	.7599	.5593	.0047	73.6	0.83
64.0	0.77	.7298	.4719	.0054	54.7	0 74
58.0	0.79	.6861	.4047	,0036	59.0	0.93
54.8	0.75	.6944	.3809	.0061	54.9	0.88
34.7	0.68	.6941	.3793	.0040	54.5	0.57

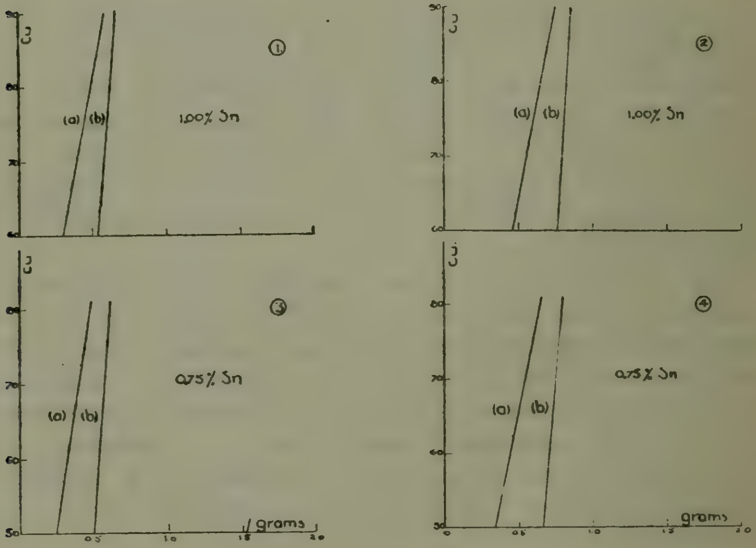

FIG. 10.

In both sets of brasses, those containing approximately 0.75 per cent. and 1.00 per cent. of tin, the amount of corrosion increases with the increase in the copper content of the test piece, while in the simple brasses the amount of corrosion increased.

This is represented diagrammatically in Fig. 10, wherein the abscissas represent the grams of corrosion, and the ordinates the percentage of copper.

Curve "a" refers to the weight of copper in the total weight of the corrosion product, which is represented by curves marked "b." From a comparison of the data in the first and in the next to the last columns of the table, it is apparent that the copper content of the corrosion product is practically the same as that of the test piece, while the large variations in the tin content of the corrosion products can be readily attributed to the very small quantities of tin present. These determinations were made in duplicate, and from the two sets of curves, "1" and "3" and "2" and "4," the general agreement is represented.

Corrosion in Sodium Nitrate Solution.

The data presented in Table XII were obtained in the electrolytic corrosion of the test pieces in a normal solution of sodium nitrate.

TABLE XII.

Percentage of copper in test piece	Percentage of tin in test piece	Grams of corrosion	Grams of copper in corrosion	Grams of tin in corrosion	Percentage of copper in corrosion	Percentage of tin in corrosion
54.7	.65	1.3280	.7262	.0089	54.7	.68
54.8	.75	1.3633	.7504	.0147	55.0	1.08
58.0	.79	1.3880	.8124	.0120	58.5	.81
64.0	.77	1.3768	.8809	.0155	64.0	1.13
73.3	.76	1.4118	1.0404	.0133	73.7	.95
77.1	.78	1.3708	1.0696	.0123	78.0	.90
81.0	.78	1.3599	1.0982	.0192	80.8	1.41
63.0	1.05	1.3767	.8676	.0141	63.0	1.03
66.7	1.07	1.4381	.9570	.0160	66.6	1.11
71.4	1.02	1.3577	.9646	.0144	71.1	1.06
74.8	.90	1.3975	1.0524	.0128	75.3	.93
77.2	.94	1.2989	.9732	.0135	75.0	1.04
86.9	.98	1.3341	1 1682	.0122	87.6	.92

The amount of corrosion seems to decrease slightly with the increase in the copper percentage of the test piece for those containing approximately 1 per cent. tin. For those containing 0.75 per cent. tin the amount of corrosion is practically constant. This is represented in Fig. 11, wherein the curves for the duplicate determination are given, thus showing that practically the same general results were obtained in both series of experiments. The data presented in Table 12 are represented by curves 1 and 3.

The corrosion in these brasses is, in general, the same as in the pure brasses of high copper content, there being a slight increase in the amount of corrosion with the decrease in the copper content. The percentage of copper in the corrosion product is practically the same as in the test piece. With one marked exception, the 77.2 per cent. copper brass in both determinations gave less corrosion and less copper in the corrosion product than the values interpolated from the values of the other brasses would indicate. The corrosion product contained less copper than the test piece, thus indicating that corrosion produces a copper-rich surface. The scale on the surface of the "kalchoids" was not so heavy as on the simple brasses, and was rather dark.

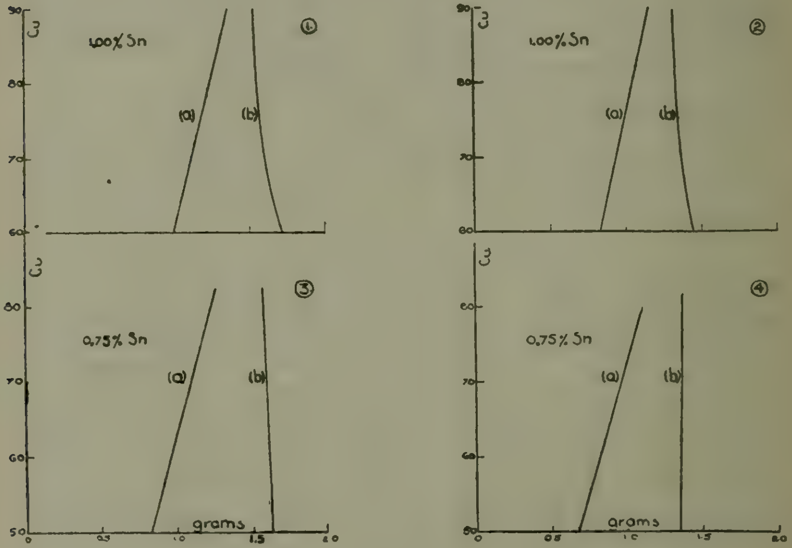

FIG. 11.

Corrosion in Sodium Sulphate Solution.

The data from the electrolytic corrosion of the test pieces in a normal sodium sulphate solution are given in Table XIII.

TABLE XIII.

Percentage of copper in test piece	Percentage of tin in test piece	Grams of corrosion	Grams of copper in corrosion	Grams of tin in corrosion	Percentage of copper in corrosion	Percentage of tin in corrosion
54.7	.65	.8564	.4715	.0041	55.1	.49
54.8	.75	.8884	.4788	.0043	54.0	.46
58.0	.79	.8458	.4888	.0063	57.8	.75
64.0	.77	.8349	.5209	.0091	62.4	1.09
73.3	.76	.8347	.6161	.0093	73.8	1.12
77.1	.78	.8322	.6425	.0053	77.2	.63
81.0	.78	.8317	.6739	.0117	81.0	1.40
63.0	1.05	.8539	.5367	.0078	62.9	.92
66.7	1.07	.8412	.5509	.0112	65.5	1.33
71.4	1.02	.8370	.5967	.0030	71.3	.35
74.8	.90	.8342	.6241	.0114	74.8	1.37
77.2	.94	.8373	.6466	.0091	77.2	1.09
86.9	.98	.8316	.7264	.0118	87.4	1.42

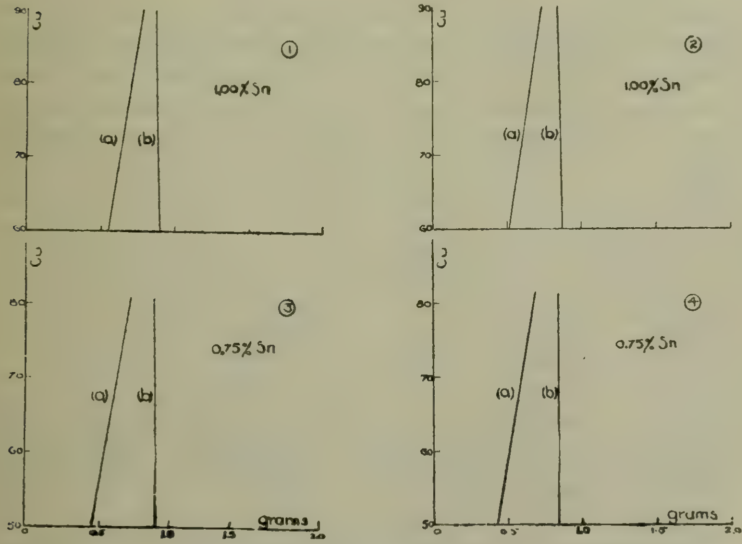

FIG. 12.

The weight of the corrosion product obtained in the sodium sulphate solution is practically the same for all the brasses examined. Neither the variation in the percentage of copper nor that of the tin affects the amount of corrosion. This is the same thing found for the copper-zinc test pieces corroded in sodium sulphate solution. Duplicate determinations were made with practically the same results, as shown clearly in Fig. 12, where the data from both series of experiments are represented. The diagrams marked "2" and "4" represent the data given in the table, and emphasize the constancy of the amount of the corrosion. The corrosion product contains apparently the same percentage of copper as the test piece. The corrosion surface of some of the test pieces was very characteristic, and Fig. 18 gives a rather imperfect idea of the appearance of the corroded surface of the test piece, containing 0.65 per cent. tin and 54.7 per cent. copper, which was corroded in the sodium sulphate solution. The same general type of corroded surface is obtained for the corrosions in the solutions of sodium nitrate and sodium chloride. The rough surfaces of the electrode are due to large, golden, rectangular crystals, which give a most beautiful effect in the sunlight.

In order to ascertain the relative amounts of corrosion in various solutions, three brasses of practically the same copper content were selected, having different percentages of tin. These were corroded in normal solutions of sodium chloride, sodium nitrate, and sodium sulphate, by passing the same current through them in series. The data are presented in Table XIV.

TABLE XIV.

Percentage of copper in test piece	Percentage of tin in test piece	Grams of corrosion					
		NaCl		$NaNO_3$		Na_2SO_4	
		1	2	1	2	1	2
73.4	0.00	.4509	.9879	.3108	.7190	.2876	.6293
73.3	0.76	.4486	.9827	.2992	.6739[10]	.2886	.6307
74.8	0.90	.4477	.9636	.2969	.6815	.2886	.6304

[10] On this test piece there remained some black patches which would increase the weight of the test piece, and thus indicate less corrosion than actually took place.

The experiment was stopped, the test pieces cleaned and weighed, the amount of corrosion being represented in the columns headed "1." The test pieces were replaced, and the experiment continued, in order to obtain a larger amount of corrosion, the amounts of which are recorded in the columns marked "2." The amount of corrosion for all three brasses is the greatest in the sodium chloride solution, the least in the sodium sulphate solution, and intermediate in the sodium nitrate solution. The brass containing the most tin corrodes in the sodium chloride solution a little less than brass containing no tin, while both of these corrode somewhat more than that brass containing 0.76 per cent. of tin. In the sodium nitrate solution, the corrosion decreases with the increase of the tin content, while in the sodium sulphate all three test pieces are corroded the same amount. It might be interesting to inquire in which of these solutions does the normal theoretical corrosion occur? If we assume that copper dissolves in the cuprous form in the sodium chloride solution, then the corrosion in the other two solutions, on the assumption that the copper dissolves as bivalent copper, is very much in excess of what it should be, and we should say the current efficiency is over 100 per cent. If we select either of the other two solutions as our standard of comparison, then we arrive at similar conclusions, for if pure copper anodes dissolve as bivalent copper, then sodium nitrate and sodium sulphate solutions should corrode the same. It is a well-known fact, however, that the deposition of copper from a copper sulphate coulometer is less than the theoretical amount, unless a little sulphuric acid is added. What should be selected as the theoretical amount of corrosion in any or all solutions, in order to calculate the so-called current efficiency, is a subject that requires further investigation.

SUMMARY.

A series of copper-zinc brasses was prepared, representing most of the different solid solutions, and these were annealed for several weeks at 400° C. to insure the presence of the stable forms at this temperature. These brasses were subjected to electrolytic corrosion in normal solutions of some of the more common sodium and ammonium salts.

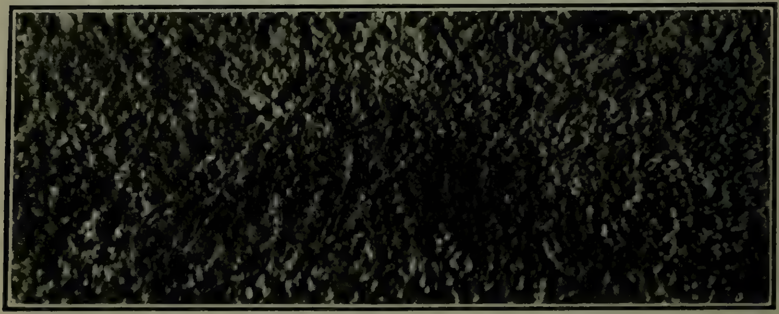

FIG. 13. (x 14).
93.5% Cu. in $NH_4 NO_3$.

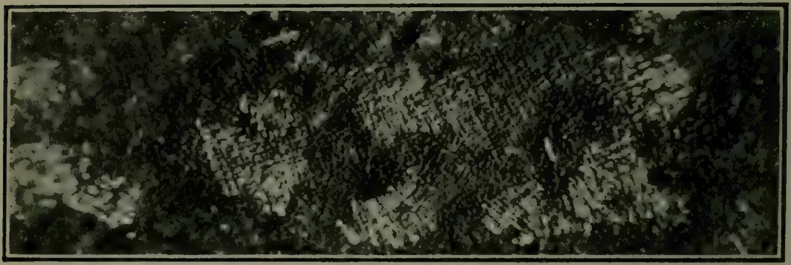

FIG. 14. (x 14).
76.3% Cu. in NaCl.

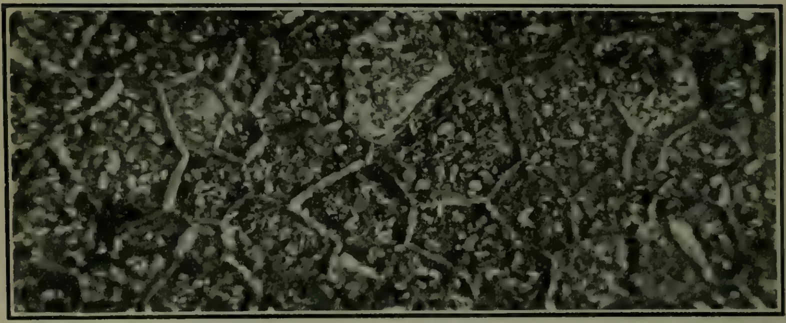

FIG. 15. (x 14).
56.8% Cu. in NaCl.

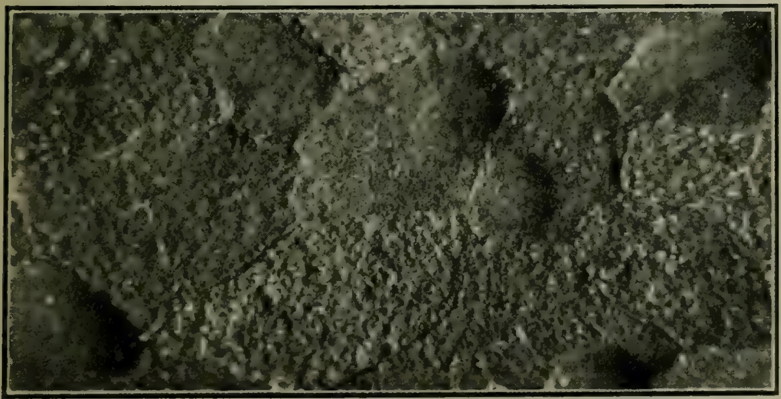

FIG. 16. (x 14).
47.6% Cu. in $NaNO_3$.

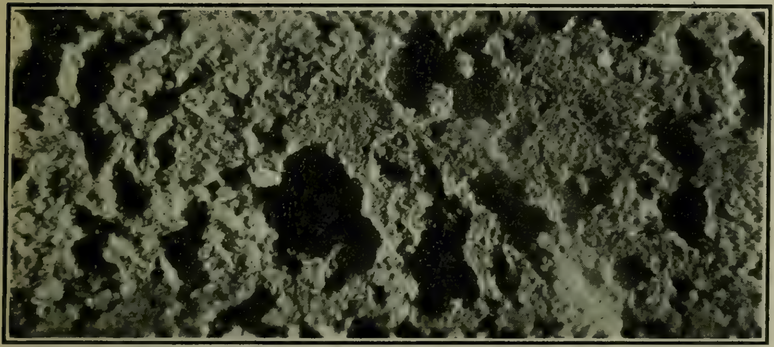

FIG. 17. (x 14).
3.1% Cu. in $NaNO_3$.

FIG. 18. (x 14).
54.7% Cu., 0.65% Sn. in Na_2SO_4

In general, the electrolytic corrosion results in the formation of a corrosion product which is practically of the same composition as the test piece for the brasses of high copper content, *i. e.*, of 50 per cent. copper and up. The corrosion product of the low percentage copper brasses is practically pure zinc. The amount of corrosion in sodium chloride decreases with the decrease in the copper content of the brass. In sodium nitrate, ammonium nitrate, ammonium oxalate, and sodium acetate solutions, the amount of corrosion increases with the decrease of the copper content of the brass for the high copper brasses, and also for the very low ones. In sodium sulphate solutions, the amount of corrosion is practically constant over the whole range of concentration of the brasses.

The α, $\alpha + \beta$ or β brasses yield corrosion products of the same composition as the brass. The presence of γ crystals seems to cause a marked decrease in the amount of corrosion, while the corrosion product from $\gamma + \epsilon$, ϵ and $\epsilon + \eta$ brasses is practically pure zinc.

A few copper-zinc-tin brasses containing small quantities of tin were subjected to electrolytic corrosion in normal solutions of sodium chloride, sodium nitrate and sodium sulphate, with the same general results as in the case of the simple brasses.

Chemical corrosions were conducted in a few solutions, but the determinations were not satisfactory.

I wish to thank Mr. David Klein and Mr. Paul E. Howe for their interest in this research and for the experimental work connected therewith.

University of Illinois,
Urbana, Ill.

DISCUSSION.

Mr. Bancroft: This work of Prof. Lincoln has brought out very clearly that there is a great multiplicity of phenomena in connection with the corrosion of alloys which we cannot predict in any way from any facts that we now know, and which we have got to get at by actual observation. One thing that occurred to me here was that if it turns out, as it undoubtedly will, that the chemical corrosion runs parallel with the electrochemical corrosion, then the statements that we have seen in various publications are wrong—that it is only Müntz metal within the limit of 2 per cent. concentration which will dissolve in sea-water without change of composition. As a matter of fact, the field covers a much wider range than that. In this electrolytic corrosion, Mr. Lincoln has not observed any effect due to the nature of the cation. We have been doing a little work on the side on the chemical corrosion of nickel in the same solutions, and we find that in the case of sodium persulphate, nickel does not corrode at all, which is exactly what we hoped would happen. On the other hand, in ammonium persulphate solution, which ought to behave in exactly the same way, nickel corrodes with great readiness, so you have a difference there due to the change of a sodium salt to ammonium salt. While it is undoubtedly true that in a great many cases the change of the cation has no effect, it is not a universal truth, by any manner of means.

When this paper is published, I hope that Prof. Lincoln will add a column giving the value of electrolytic efficiency in percentages. I can grasp a percentage efficiency much better than I can reason out conclusions based on grams corrosion for an indefinite time with an indefinite current.

PROF. RICHARDS: I think that while this is undoubtedly a very important scientific contribution, studying the use of the separate salts, yet the paper would have gained in the value of its applications if sea-water itself had been used as one of the agents for corrosion. While the separate ingredients of which sea-water is composed may have a certain action upon the metal, their combination might have a different action, and the industrial application of these alloys on ships is so important that the relative rate of corrosion by actual sea-water itself would have added an important column to the investigation.

MR. G. G. GROWER: I have had occasion to make some experiments on chemical corrosion without any external source of current, and, as near as I can judge, the results were somewhat parallel to those of Mr. Lincoln for electrolytic work. I did nothing quantitative in the work at all, only qualitative, as applied in the commercial alloys as produced in the ordinary brass concerns; I worked with sea-water taken from Long

Island Sound, and with dilute sulphuric acid. The results from sulphuric acid were quite definite, compared with what they were for sea-water; but, at the same time, they appear to be more or less parallel, and it is quite surprising to see that pure copper and the alloys rich in copper were corroded a great deal more than the Müntz metal or alloys in the neighborhood of 2 : 1.

The solution got quite distinctly blue, even on pure copper, with sulphuric acid, and also in the rich copper alloys, whereas with the Müntz metal the solution is absolutely colorless—to all appearance no corrosion at all. We also made some chemical tests of the solution obtained, and it bore out the same thing—the corrosion exceedingly slight on Müntz metal and those alloys in that neighborhood, whereas those richer in copper were much more vigorously corroded, even pure copper.

A lecture delivered at the Eleventh General Meeting of the American Electrochemical Society, in Philadelphia, Pa., May 3, 1907; President Carl Hering in the chair.

ELECTRIC CONDUCTION.

By Charles P. Steinmetz.

The subject of my lecture is Electric Conduction. I desire to make it a little broader than announced, and speak not only of conduction of gases and vapors, but of conduction in general. When electric power flows through a circuit, we find phenomena taking place outside of the conductor which directs the flow of power, and also inside thereof. The phenomena outside of the conductor are conditions of stress in space which are called the *electric field,* the two main components of the electric field being the electromagnetic component, characterized by the circuit constant *inductance* L, and the electrostatic component, characterized by the electric circuit constant *capacity.* Inside of the conductor we find a conversion of energy into heat; that is, electric power is consumed in the conductor by what may be considered as a kind of resistance of the conductor to the flow of electric power, and so we speak of *resistance* of the conductor as an electric quantity, representing the power consumption in the conductor.

It is the nature of the human mind that when we find a mass of different phenomena, we try to classify it into definite and well-defined groups, although we begin now more and more to realize that there are no distinct classes in nature, but a gradual transition from type to type. So also electric conductors have been classified and divided into distinct groups, and then treatises written to discuss whether a conductor belongs to one class or another.

The *first class of conductors* are the *metallic conductors.* They can best be characterized by a negative statement—that is, metallic conductors are those conductors in which the conduction of the electric current converts energy into no other form but heat. That is, a consumption of power takes place in the metallic conductors by conversion into heat, and into heat only. Indirectly, we may get light, if the heat produced raises the temperature high enough to get visible radiation, but this radiation is produced from heat, and directly the conversion of electric energy takes place into heat. These metallic conductors cover, as regards their specific resistance, a rather narrow range, between about 1.6 microhm-centimeters (1.6×10^{-6}) for copper, to about 100 microhm-centimeters for cast-iron, mercury, high-resistance alloys, etc. They therefore cover a range of less than 1 to 100.

A characteristic of metallic conductors is that the resistance is approximately constant, varying only slightly with the temperature, and this variation is a rise of resistance with increase of temperature—that is, they have a positive temperature coefficient. In the pure metals, the resistance apparently is approximately proportional to the absolute temperature—that is, the temperature coefficient of resistance is constant, and such that the resistance plotted as function of the temperature is a straight line which points towards the absolute zero of temperature, or, in other words, which prolonged backwards towards falling temperature, would reach zero at —273° C., as illustrated by curves I on Fig. 1.

In alloys of metals we generally find a much lower temperature coefficient, and find that the resistance curve is no longer a straight line, but curved more or less, as illustrated by Curve II, Fig. 1, so that ranges of zero temperature coefficient, as at A in Curve II, and even ranges of negative temperature coefficient, as at B in Curve II, Fig. 1, may be found in metallic conductors which are alloys, but the general trend is upward. That is, if we extend the investigation over a very wide range of temperature, we find that even in those alloys which have a negative temperature coefficient for a limited temperature range, the average temperature coefficient is positive for a very wide range of temperature—that is, the resistance is higher at very high and lower at very low temperature, and the zero or negative coefficient occurs at a local flexure in the resistance curve.

The *conductors of the second class* are the *electrolytic conductors*. Their characteristic is that the conduction is accompanied by chemical action. The specific resistance of electrolytic conductors in general is about 1,000,000 times higher than that of the metallic conductors. They are either fused compounds, or solutions of compounds in solvents, ranging in resistivity from 1.3 ohm centimeters, in 30 per cent. nitric acid, to about 10,000 ohm centimeters in pure river water, and from there up to infinity (distilled water, alcohol, oils, etc.).

Characteristic of the electrolytic conductors is the negative temperature coefficient of resistance; the resistance decreases with increasing temperature—not in a straight, but in a curved line, as illustrated by Curve III in Fig. 1.

I found that when dealing with electrical resistances, in many cases it is more convenient and gives a better insight into the character of the conductor, by not considering the resistance as a function of the temperature, but the voltage consumed by the conductor as a function of the current under stationary condition. In this case, with increasing current, and so increasing power consumption, the temperature also rises, and the curve of voltage for increasing current so illustrates the electrical effect of increasing temperature. The advantage of this method is that in many cases we get a better view of the action of the conductor in an electric circuit by eliminating the

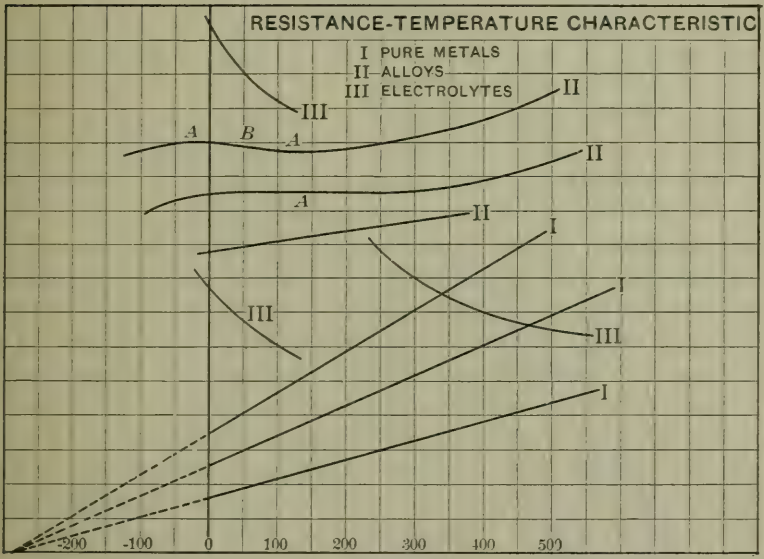

FIG. 1.

temperature, and relating only electrical quantities with each other. Such volt-ampere characteristics of electric conductors can easily and very accurately be determined, and, if desired, by the radiation law approximate values of the temperature be derived, and therefrom the temperature-resistance curve calculated, while a direct measurement of the resistance over a very wide range of temperature is extremely difficult, and no more accurate.

In Fig. 2, therefore, are shown such volt-ampere characteristics of conductors. The dotted straight line is the curve of absolutely constant resistance, which does not exist. Curves I and II show characteristics of metallic conductors, Curve III of electrolytic conductors. As seen, for higher currents I and II rise faster, and III slower than for low currents.

As a further class of conductors, very frequently the so-called insulators are considered—that is, conductors which have such a very high specific resistance that they cannot industrially be used for conveying electric power, but, on the contrary, find a use for restraining the flow of electric power to the desired conductor, or path, by separating the conductor from the surrounding space by such an insulator. The insulators also have a conductivity, but their specific resistance is extremely high. To illustrate, for instance, the specific resistance of fiber is about 10^{12}, of mica, 10^{14}, of rubber, 10^{16} ohm-centimeters, and still higher that of air, etc.

The next class of conduction is the conduction of gases and vapors. In this field, in recent years, an enormous amount of theoretical speculative work has been done by extending the ionic theory, which originally started in the investigation of electrolytic conductors, to the conduction of gases and vapors.

The ionic theory explains electric conduction as a convection of electrostatic charges. While this theory may be useful in picturing certain phenomena, we must realize that, like all theories, it is a hypothetical speculation, and not an empirical fact, that the explanation of phenomena given by the theory is extremely crude, crude in direct proportion to our limited knowledge of experimental facts, and that the same fate awaits the ionic theory which has overtaken all previous theories—to be overthrown and discarded with our increasing knowledge of facts; or, perhaps, as we now prefer to do, to avoid the appearance of cataclysmic changes, to be amended and re-amended, until it has lost all resemblance to its previous form.

As it is my intention here to discuss the empirical facts of electric conduction, I shall not use the ionic theory, nor any other fantastic metaphysical speculation, since I consider it vicious and unscientific to express facts in the form of their interpretation by any prevailing theory, no matter how universally-accepted this theory may appear. In experimentally determining so-called "facts," so many sources of accidental and constant errors exist, that it appears inexcusable to vitiate the facts still further by mixing them up with metaphysical speculations.

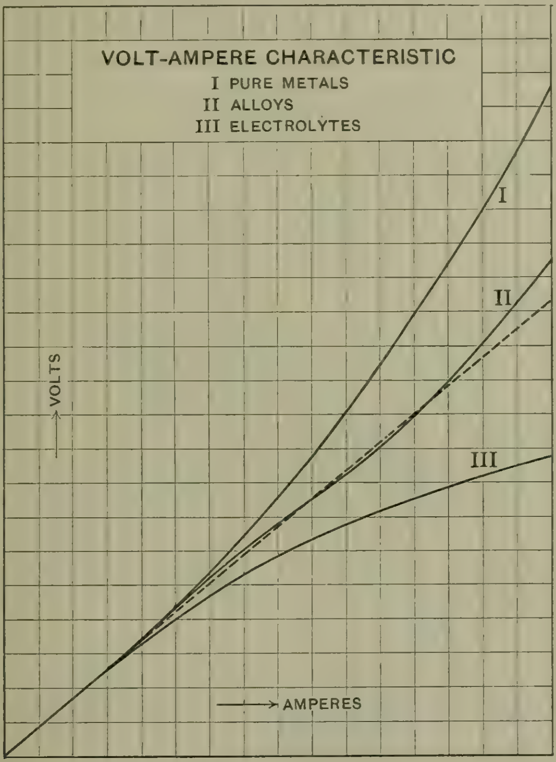

FIG. 2.

While the ionic theory has undoubtedly contributed to the advance of our knowledge, especially in the field of electrolytic conduction, it has often appeared to me questionable whether in the study of conduction of gases and vapors, the ionic theory has not rather retarded progress than advanced it. While an enormous amount of experimental theoretical work has been done through many years, by numerous scientific investigators, on the conduction of gases, and the most intricate and abstruse theories devised, some of the very simplest questions, as, for instance, how, in the discharge of a Geissler tube, the terminal voltage varies with the current, which is the first question an engineer would ask, stand unanswered to-day.

In gases and vapors we find two distinct classes of conduction, the electric discharge and the electric arc. If you have two solid or liquid terminals, separated by a gas or vapor, and pass a current between these terminals, then this current either passes through the gas or vapor which fills the space between the terminals—electric discharge, as static spark, Geissler discharge, or the current makes its own conductor by evaporating and converting into vapor the material of the electrodes, and so producing its own vapor conductor—electric arc. So you see, in the *electric discharge* the passage of the current is through the material filling the space between the electrodes; in the *arc* the passage of the current is through a vapor conductor, a vapor stream which is produced by and from the material of the electrode. Incidentally, one of the results of this phenomenon is that the electric discharge is usually discontinuous, while the arc must always be continuous.

The spectrum of the electric discharge, then, is the spectrum of the gas or vapor filling the space; the spectrum of the arc is that of the material of the electrodes. The difference between Geissler discharge and arc, I illustrate here on this mercury tube (Fig. 3). This tube[1] has four mercury terminals, a, b, c, d. It is very well exhausted, while heating it to drive off all residual gas, washed out with hydrogen, and then filled with mercury. Traces of hydrogen are left in the tube, a very small fraction of 1 mm. in pressure. This is not essential, but is desirable for lecture experiment, since with an absolutely perfect vacuum the voltage required to produce the electric discharge would be so

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[1] For complete description of tube and its dimensions and exhaustion, see appendix, p. 111.

high as to be beyond the means available here. I have, therefore, intentionally left a trace of hydrogen in the tube, to bring the voltage required for the Geissler discharge down to 2,000.

An alternating e. m. f. of about 2,000 volts is applied to the terminals, b and d, of the tube, through a step-up transformer, AB, as illustrated in Fig. 3. By a reactance, X, in the primary of the transformer, the discharge current is limited to a very small value, about ¼ ampere. As you see, after closing the circuit, a striated Geissler discharge fills the tube between terminals b and d, a distance of 20 inches, of the green color of the mercury spectrum.

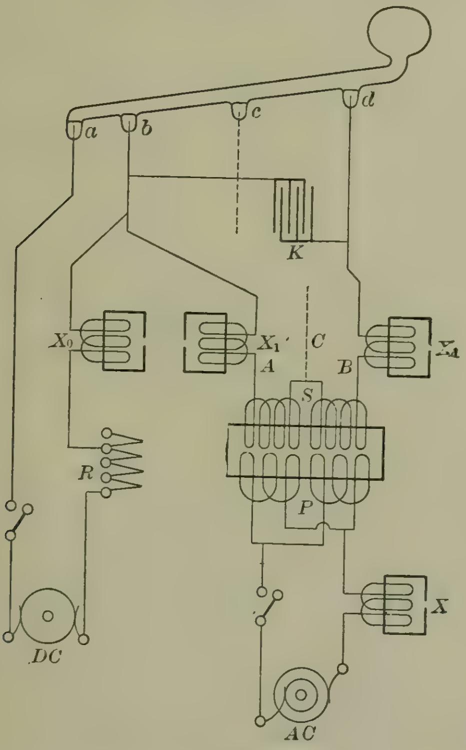

FIG. 3.

Now I connect terminals a and b to a source of direct current, DC, of 250 volts, with sufficient resistance, R, in series to limit the current to about 3 amperes, and some reactance, X, to steady the current. In tilting the tube so that some mercury overflows from b to a, I close the circuit momentarily, and so start an arc between terminals a and b. You notice, in this arc, one of the terminals, the positive, is quiet; on the other terminal, the negative, an intensely bright spot is rapidly running around. This is the so-called "negative spot," at which the mercury vapor is produced which passes from negative to positive as a vapor stream, and so acts as the conductor carrying the current.

You see here simultaneously in the same tube a Geissler discharge through mercury vapor, and a mercury arc. The Geissler discharge fills the whole tube, is striated, with the striations waving along the tube in the usual manner, while the terminals are quiet. The arc is a steady stream of uniform intensity, in the present case not quite filling the whole tube, is of far greater brilliancy than the Geissler discharge, due to the higher current, and the negative terminal is violently agitated; the vapor density in the arc is far higher than in the Geissler discharge, so masses of mercury issue from the arc stream, and condense in the tube outside of the arc, as you see—that is, the arc produces its own vapor stream.

Now I connect an electrostatic condenser, K, across the terminals of the Geissler discharge, b and d. Immediately the striated green Geissler discharge disappears, and its place is taken by an intensely bright condenser discharge of reddish color—the red mercury arc of the condenser discharge. The spectroscope still shows the usual mercury lines, but shows, in addition, a considerable number of bright lines in the red which are not visible in the ordinary mercury arc, and only faintly visible in the mercury arc when running at high current densities. Of these red lines, most prominent is one in the dark red, and two closely adjacent in the bright red. During the red condenser discharge, the current in the primary, P, of the transformer is 6 to 8 amperes, the ratio of transformation in this transformer is 20, and the current supplied by the transformer secondary, S, therefore about one-third ampere, and still, as you see, the copper wire connecting the tube with the condenser becomes incandescent and melts off, which requires over 20 amperes. We have here an oscillating condenser discharge of extremely high frequency, hundred thousands of cycles per second—that is, oscillations of extremely short duration, but of hundreds of amperes, alternate with long periods of rest, and the heating effect, which depends upon the average square of current, is very great. Very commonly, when producing the red condenser discharge, the seals of the mercury tube crack, by the platinum wire (40 mils diameter) getting hot and cracking the glass. To exhibit this phenomenon in its greatest brilliancy without danger to the tube, it is therefore advisable to use two or three platinum wires of 40 mils diameter in multiple as leading-in wires.

This red condenser discharge gives the high-temperature spectrum of mercury vapor—that is, the passage of current through highly superheated mercury vapor; the duration of the discharge is so short that no time exists to project sufficient mercury vapor through the tube to carry hundreds of amperes without excessive heating.

The red condenser discharge does not show any striations, but shows considerable agitation of both electrodes b and d—that is, apparently is of the nature of an alternating arc at high voltage through highly superheated mercury vapor.

If we had somewhat higher voltage available, I could show you all three phenomena in the same tube, by connecting the middle terminal, C, of the transformer to the terminal, c, of the mercury tube, which is intended for this purpose, and connecting the condenser between c and d. Then a to b show the green mercury arc, b to c the green striated Geissler discharge, and c to d the red condenser discharge. This requires about 150 to 200 volts at the primary terminals P, at a 20 ÷ 1 transformer ratio.

We see, herefrom, that current can traverse a gas or vapor in two different manners—either by using the gas filling the space as a conductor, the electrical discharge as represented by the static spark at atmospheric pressure, or by the Geissler discharge at reduced pressure, or the current can traverse the vapor as arc, then making its own conductor by producing a vapor stream from the terminals, which then carries the current. In the latter case, the spectrum of the phenomenon is independent of the gas which fills the space between the electrodes, but is the spectrum of the electrodes, while in the former case it is the spectrum of the gas which fills the space. In this case, here experimentally illustrated, with mercury vapor filling the space between mercury electrodes, the Geissler discharge gives the same spectrum as the arc, but still, as you see, the two phenomena are distinctly different; the one is a striated discharge, the other a steady stream, and the two phenomena cannot be gradually changed into each other, but if in the Geissler discharge current and voltage are gradually raised, suddenly an arc flashes up, the current suddenly increases many-fold, the striations disappear, and a bright, uniform flash passes through the tube, while violent agitation occurs at the electrodes, and by again lowering the voltage, the arc suddenly extinguishes, the electrodes become quiet, and the tube is filled with the striated Geissler discharge. The arc in this case is usually rectifying—that is, only every second half-wave passes.

In the following I shall mainly discuss arc conduction, since even the most fundamental engineering data on Geissler tube discharges are unknown, as stated above, while on arc conduction considerable data are available as the result of the work of electrical engineers, to whom the arc has been of more interest, due to its greater commercial importance.

I here produce the ordinary carbon arc at atmospheric pressure, by separating in a hand lamp two carbon electrodes from each other, while connected into a 250-volt direct-current circuit, with sufficient resistance in series to limit the current to about 3 to 4 amperes, and some inductance to steady the arc (0.6 henrys). As you see, you get a very brilliant light from the lower terminal, which is positive, and becomes highly incandescent, some light from the upper, or negative, terminal, but practically no light from the arc stream or vapor conductor, which carries the current across the gap between the electrodes—that is, the spectrum of the carbon vapor is almost non-luminous.

The question now is, which one of the electrodes, the positive or the negative, produces the arc vapor? We find the positive terminal is by far the hotter. It consumes more rapidly, about twice as fast, in open air, as the negative, and herefrom the conclusion has frequently been drawn that the positive terminal supplies the conducting vapor to the arc stream. If, however, we enclose the carbon arc as nearly air tight as possible, we find the consumption of carbon greatly reduced (to one-tenth or one-twentieth of its former value), and the terminals consume less unevenly; the positive may even consume less than the negative, but the arc still has the same character. It follows, herefrom, that of the total amount of carbon consumed in an open-air arc, only a very small part is required to produce the carbon-vapor stream, which carries the current, and that therefore no conclusions whatever can be drawn from the rate of consumption of the carbon, on the question which of the electrodes feeds the arc stream, but the greater rate of consumption of the positive carbon in the open arc is the obvious result of the higher temperature, which produces more rapid combustion of the positive terminal. Which electrode in the carbon arc produces the arc stream could therefore be determined only by enclosing the arc in an atmosphere which does not combine with carbon. Argon or helium may do this, but I do not know of any other gas which does not react with carbon at arc temperatures.

I now replace the lower positive carbon with a magnetite electrode, as used in the luminous arc or magnetite lamp,[2] leaving carbon as negative electrode.

You see, the arc remains the same as before—a non-luminous carbon-arc flame, in this case colored slightly yellow by the omnipresent sodium, a large production of heat at the positive, which melts at the surface, but the arc flame does not show the spectrum of iron or titanium—that is, no material enters the arc flame from the positive, or, in other words, the positive terminal does not supply the vapor conductor.[3]

I now reverse the current, make the upper carbon electrode positive, the lower magnetite electrode negative, start the arc, and you see the bright, intensely-brilliant white arc of iron and titanium; the spectrum of the arc flame now shows the lines of iron and titanium, and even the character, the voltage consumed, and the shape of the arc have changed; the arc looks like a blast

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[2] A thin iron tube filled with a mixture of magnetite with some rutile and some chromite.

[3] Except indirectly: if the positive contains a material which boils much below the temperature of the arc stream, that is, of the temperature of the boiling point of the material of the negative terminal, and the positive is sufficiently small to get very hot, material may enter the arc stream by heat evaporation from the positive and then give its color and spectrum to the arc stream. This spectrum, however, decreases or even disappears by cooling the positive so as to keep its temperature low, while the spectrum of the negative terminal never disappears from the arc stream, no matter how energetically the negative terminal is cooled.

flame issuing from a small spot of the negative and diffusively surrounding the positive, and this negative spot tends to run around rapidly over the surface of the melted pool on the negative, just as we have seen it in the mercury arc. That is, this negative spot is the focus from which the current issues, at which the arc vapor is produced, and from which the vapor stream which carried the current, and so forms the arc conductor, starts.

I now replace the carbon positive with a copper rod, start the arc, and, you see, nothing has changed, but the arc is the same iron-titanium arc, the shape is the same, also the voltage, etc. The only difference is that the bright incandescent spot at the tip of the positive carbon does not appear on the copper positive, since the copper is such a good conductor of heat as to carry away the heat which is produced there; if the copper positive is too small to conduct the heat away, it melts off.

I now once more reverse the current, make the copper negative and the magnetite positive, and start the arc, and you see the less luminous green copper arc, while the lines of iron and titanium have faded in the spectrum, although the magnetite electrode, as positive, now is far hotter than before.

It follows, herefrom, that with the electrodes shown here, and with all electrodes, without exception, which so far I have had occasion to investigate, the negative terminal feeds the arc flame—that is, produces the arc vapor, and the spectrum of the arc conductor thus is the spectrum of the negative electrode, but the positive electrode does not participate in the arc conduction, but is immaterial, and the hot spot appearing at the tip of the positive terminal with sufficiently refractory materials has nothing to do with the phenomenon of arc conduction, but is merely an effect of the heat produced at the positive.

In this experiment, we had 250 volts direct current available in the circuit, and, as you saw, had no difficulty to draw the arcs out to a length of an inch and more.

I now bring the magnetite and copper electrodes in contact with each other, and connect the lamp into the 60-cycle alternating current circuit, of 600 to 700 volts, with sufficient reactance in series to limit the current. Trying now to start an alternating arc, by slowly separating the terminals, we see that as soon as the terminals separate the least bit—1-64 inch, or less—the circuit opens. I try this over and over again, with the same result. That is, 600 volts alternating e. m. f. cannot maintain an arc between magnetite and copper, no matter how short, while 250 volts direct current can maintain a long steady arc. I now change the alternating circuit so as to get 1,200 volts in the circuit, and still we get the same result—1,200 volts 60-cycles alternating current cannot maintain even a short arc between magnetite and copper terminals, while 250 volts direct current maintained a long arc. The same experiment may be tried with almost any other material as electrode.

It seems, herefrom, that an alternating e. m. f. can in general not maintain an arc, but that the arc is essentially a direct current phenomenon, and requires for its maintenance a continuous applied e. m. f.

We know that an alternating arc can be maintained between carbon electrodes, and alternating-current, carbon arc lamps are extensively used. Carbon, however, and also some very refractory substances, mainly carbides, make an exception.[4]

The explanation hereof I have given in several previous papers,[5] and in reality is obvious, as we have seen. As the arc conductor, or vapor which carries the current, is produced, it issues from the negative electrode as vapor stream or blast. With an alternating arc, at the end of the half-wave, the current falls to zero, the vapor stream so ceases, and for the next half-wave a vapor stream of opposite direction would be required—that is, a spot on the other terminal raised to the boiling point, and sufficient material evaporated to carry the current. This requires energy and so high voltage. That is the alternating arc goes out at the end of each half-wave, and has to be restarted, in opposite direction, at the beginning of every half-wave, by a static spark. Very clearly this was illustrated by stroboscopic photographs of metal arcs, shown by Prof. Lombardy at the International Electrical Congress, at St. Louis. By using sufficiently high voltage (I believe 6,000

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[4] This shows the serious error, which many investigators committed, in using the carbon as typical arc, and drawing general conclusions on arc conduction from the phenomena of the carbon arc.

[5] Transactions International Electrical Congress, 1904: "The Electric Arc."
" A. I. E. E., 1905: "Constant Current Mercury Arc Rectifyer."
" " 1906: "Light and Illumination."

volts) an alternating arc was maintained between metal terminals, and the photograph shows at the beginning of every half-wave a static spark, sharply defined, very brilliant and of the usual zigzag shape, passing between the electrodes. This gradually thickens, while its boundary gets fluffy and indistinct, and it assumes the usual form of an arc stream, as I showed it in the magnetite arc. Towards the end of the half-wave, it gradually fades out and disappears, and at the beginning of the next half-wave a new static spark has to start the arc again.

The alternating voltage required to maintain an arc, therefore, is the voltage required to jump an electrostatic spark between the terminals, at the beginning of every half-wave, through the remaining vapor stream—that is, at the temperature of the boiling point of the electrodes. The voltage required to jump a static spark across the space depends upon the temperature, and decreases greatly at high temperature, so that at some temperature, not very far below the temperature of the carbon arc, the spark voltage falls below the arc voltage—that is, any voltage which is sufficient to maintain an arc, is sufficient to start it at every half-wave. Carbon and some other very refractory materials can thus maintain an alternating arc. But even with the alternating carbon arc, especially between hard carbons, which produce less vapor, this phenomenon of restarting of the alternating arc at every half-wave is noticeable in the oscillogram of current and voltage, by a high voltage peak at the beginning of every half-wave, following a period of practical extinction of the current. Electrically, this phenomenon appears as a distortion between current and e. m. f. wave, and so as a decrease of the power factor.

In the magnetite arc, whose temperature is much lower than that of the carbon arc, about 2,000 volts are required to maintain an alternating arc, and at the low temperature of the mercury arc, a still many times higher voltage, which, however, is reduced if the temperature of the mercury vapor is greatly increased, as, for instance, in the condenser discharge. That is, the red mercury arc in superheated vapor occurs at a lower voltage than a green, low-temperature, alternating, mercury arc.

Now I shall show another experiment, illustrating the production of the arc conductor from the negative electrode. I connect a copper rod through a moderate resistance—10 ohms—with the upper or positive copper terminal of the magnetite arc. The arc is not running, but the direct current potential, 250 volts, is on the circuit. I touch this auxiliary anode to the lower magnetite terminal, withdraw it, and so start an arc between the auxiliary terminal and the negative main terminal. As soon as the arc flame even approaches the main positive terminal, the arc jumps from the auxiliary copper anode to the main copper anode, so short-circuiting the resistance in the auxiliary anode circuit, although the two anodes are far from contact with each other. That is, as far as the arc flame reaches, the space is conductively connected with the negative terminal, and the arc so can jump from anode to anode, or divide itself between several anodes, in proportion to their resistance and temperature. This experiment of shifting the arc from anode to anode always succeeds.

Now I connect the same auxiliary terminal through the same resistance with the lower, or negative, magnetite terminal, as auxiliary cathode or negative terminal, and start an arc between the auxiliary cathode and the copper anode by bringing them in contact and separating them. I can draw out this arc so that it wraps itself around the negative magnetite terminal, and still the current goes to the auxiliary copper rod and through the 10 ohms resistance, rather than to enter directly through the lower magnetite terminal. Even by bringing the auxiliary cathode in contact with the lower main cathode and then separating them, the arc usually remains at the auxiliary cathode. Occasionally it remains at the main cathode, and if you watch the phenomenon, you see the negative spot running around the surface of the cathode; if now, during the contact of the auxiliary cathode with the main cathode, the negative spot happens to run off the copper rod onto the magnetite electrode, then, when withdrawing the copper rod, the arc remains on the magnetite, otherwise it follows the copper, but in any case it goes to the one or the other, but never, under the conditions of this experiment, divides itself between two cathodes. It follows, herefrom, that the arc cannot jump from cathode to cathode as it can jump from anode to anode, but it must be continuous at the cathode or negative terminal. This continuity of the arc at the negative spot is an obvious and necessary result of the production of the arc stream from the negative terminal. The conductor which carries the current issues from the spot on the negative, and so only this spot is as negative connected with everything else within the reach of the arc flame as positive, and any other point, to be negative terminal, would have to produce an arc stream—that is, requires to start the vapor blast by the expenditure of energy, as by an electrostatic spark. And, indeed, the negative spot can jump from terminal to terminal, if, by some high-voltage oscillation entering the circuit, the energy of starting the arc blast at a new place is provided. This occasionally happens in high potential mercury arc rectifiers.

The continuity of the electric arc at the negative terminal, resulting from the production of the arc conductor from the negative electrode, can be used for changing alternating current to direct current by rectification.

In its crudest form, I show you here such a rectifying device, consisting of a lower magnetite electrode and two upper copper electrodes pointing towards the magnetite electrode, The two upper electrodes are connected to the outside terminals of a high-potential transformer coil, about 2,000 volts, through inductances. and the lower magnetite electrode connects through a high inductance, and an electrolytic cell to the neutral or center of the transformer coil—that is, the usual rectifier connection, as sketched diagrammatically in Fig. 4. By bringing the magnetite electrode in contact with the copper electrodes, and so starting the arc, the electrolytic cell exhibits the unidirectional character of the current from the magnetite electrode by the rapid evolution of hydrogen and oxygen. I am sorry that the time has become too late to connect up this appliance and exhibit its rectifying action. It is, however, well known, and extensively used commercially for constant potential, as well as for constant current rectifiers, in the former case impressing a constant alternating potential, in the latter a constant alternating current upon the rectifier. Commercially, always mercury arcs in a vacuum are used—that is, a vacuum tube containing one mercury terminal as common negative or cathode, and two graphite terminals as anodes. The advantage of the mercury arc rectifier is the far greater voltage range through which rectification occurs, due to the lower temperature of the mercury arc, as explained above, and the constancy of operation, there being no consumption of electrodes in a vacuum. The electrical action of the mercury-arc rectifier, and the function of the reactive coils, I have explained in previous papers.[6]

Another useful employment of this feature of the arc, to be a unidirectional conductor, is made in the so-called "non-arcing" lightning-arrester spark terminals. A large number of spark gaps, between metal cylinders, are connected between the line and the ground, so that the normal voltage of the machine or the circuit cannot jump across the spark gaps, but any excess voltage, as lightning, jumps across and discharges to ground. In these metal cylinders, alloys of metals of low boiling point, as zinc, are used, and in an alternating-current circuit a high voltage discharge over the lightning arrester—that is, between the non-

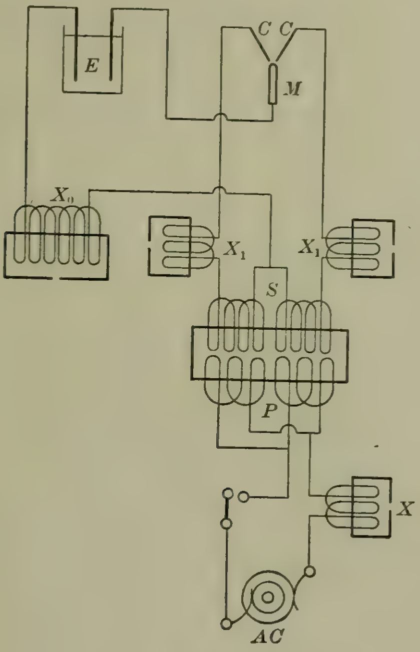

FIG. 4.

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[6] A. I. E. E. Transactions, 1905: "Constant Current." "Mercury Arc Rectifier."

arcing metal cylinders starts an arc, but this arc extinguishes at the end of the half-wave, and so the circuit opens again.

We come now to the arc as conductor—that is, the resistivity of the arc flame. With an arc, we have in the arc flame a vapor conductor between the two terminals; but that is not all. There must be something going on at the terminals also, because the vapor stream is produced at and from the material of the negative terminal, and that takes energy; considerable heat is produced at the positive terminal, which takes energy also. Hence there must be a drop of potential at the electrodes of the arc, representing the power consumption by producing heat and mechanical motion of the vapor stream. It is reasonable to assume that the amount of vapor which carries the current, and therefore the section of the arc stream at constant pressure, is proportional to the current in the arc—that is, at constant arc vapor pressure, the arc section is proportional to the current. That means the diameter of the arc stream, and thus the circumference of the arc stream, is proportional to the square root of the current, always assuming constant vapor pressure, as in arcs in air. The circumference being proportional to the square root of the current, the total surface of the arc stream, as circumference times length, is proportional to the length of the arc into the square root of the current. All the energy consumed in the arc must be radiated from the surface of it; so the energy radiated is proportional to the surface from which it radiates. The energy radiated, however, is the energy consumed, ei, where e is the electromotive force consumed by the arc flame, i is the current, and so you get a proportionality:

$$ei = cl\sqrt{i}$$

or

$$e = cl\ e = \frac{cl}{\sqrt{i}}$$

or

$$e^2 i = \text{constant.}$$

That is, the voltage consumed by the arc flame is proportional to the arc flame length, and inversely proportional to the square root of the current. This can be only an approximate formula, because it assumes the surface of the arc stream as a cylindrical surface, which it obviously is not; it moves and varies and flares around. As a rough approximation of the volt-ampere relation of the arc flame, this expression agrees fairly well. It is a cubic hyperbola.

From this expression,

$$e = \frac{cl}{\sqrt{i}}$$

follows the resistance of the arc stream,

$$R = \frac{e}{i} = \frac{cl}{i\sqrt{i}}$$

and therefrom the specific resistance,

$$r = \frac{Rs}{l} = \frac{C}{\sqrt{i}}$$

since the section s is proportional to the current, as discussed above.[7] That is, the resistivity or specific resistance of the arc vapor is inversely proportional to the square root of the current in the arc. You get, then, a resistance curve of the arc conductor which is a function of the current, the resistance decreasing with increase of current. Here the use of the volt-ampere characteristic, to express the electrical relations in the arc, is specially advantageous. As stated, at the terminals there must be also a drop of voltage; and since the amount of vapor produced was assumed as proportional to the current, and the heating effect at the positive proportional thereto also, we can assume that the amount of power consumed at the terminals is also proportional to the current. The power is counter-electromotive force or potential drop at the terminals times current, and the power being proportional to the current, you see that the potential drop at the terminals must be a constant, independent of current strength and arc length.

This agrees with experience; you find that in the mercury arc there is a constant potential difference at the two terminals of 13 volts, which rises to about 16 volts with cadmium and zinc, with a higher boiling point; rises to 30 volts in the magnetite arc, and to something like 36 volts in the carbon arc, in which the phenomenon is much more complex, however, because the carbon does not melt.

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[7] On the volt-ampere relations of arcs, see A. I. E. E., 1906; and also Transactions International Electrical Congress, 1904.

Considering only the conductivity or resistivity of the arc vapor or arc stream, we get volt-ampere characteristics, like those shown as curves I and II in Fig. 5—that is, with increasing current, i, the voltage decreases.

In the mercury arc, in a vacuum, we have a very long arc, with very moderate voltage, while an open-air arc is short and requires high voltage. For instance, it takes 80 volts to maintain a ¾-inch magnetite arc at 4 amperes. At 4 amperes, 80 volts in a glass tube like this (1 inch in diameter) maintains a mercury arc of about 5 feet in length—60 inches. But while for the same voltage, the mercury arc in a vacuum is very much longer, it also is much larger in diameter, and if you calculate the specific

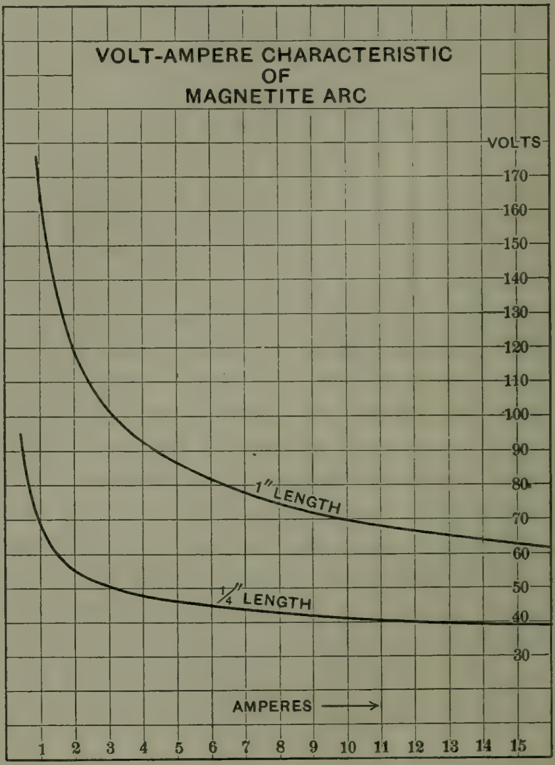

FIG. 5.

resistance of the arc stream or the arc vapor, we find very little difference between the specific resistance of the long mercury arc of large diameter, in a high vacuum, and the short but thin magnetite arc at atmospheric pressure. At 4 amperes, the specific resistance of the magnetite arc is about 4 ohm-centimeters, and of the mercury arc about 2 ohm-centimeters. It varies greatly with the section of the stream and with the current density, and so a mercury arc of about ½ inch diameter would give, at 4 amperes, the same specific resistance of the vapor conductor as an open-air magnetite arc.

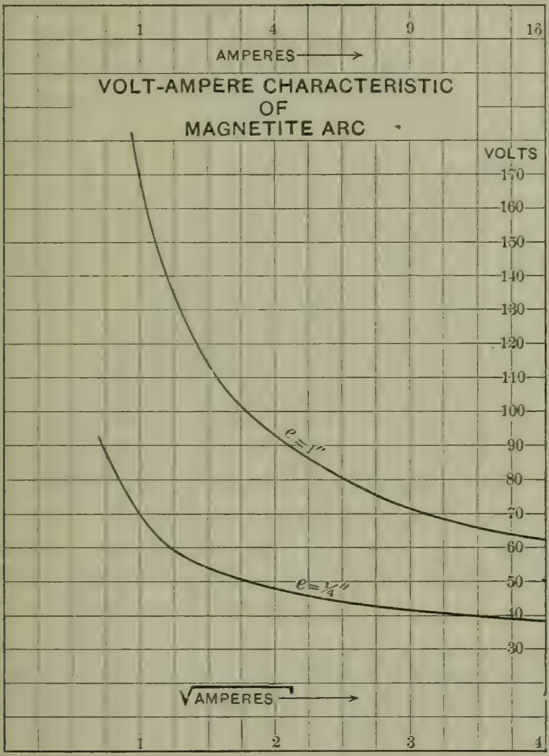

Fig. 6.

Regarding Geissler tube conduction, very few data are known, as I said before. We don't know the specific resistance of this discharge, but some data were published recently, in a paper by Mr. Moore on his method of lighting, and from these it follows that under his condition (nitrogen in a glass tube about 1¾ inches diameter, 0.1 mm. gas pressure, and alternating 60-cycle current of 0.3 ampere) he got a specific resistance of about 80 ohm-centimeters. Since the specific resistance of the Geissler tube probably decreases with increase of current, you see that for higher currents the specific resistance of the Geissler tube probably is of the same magnitude as arc conduction, and this magnitude is in the range of electrolytic conduction. That is, the specific resistance of the arc flame is of the same magnitude as that of electrolytic conductors, or about 1,000,000 times higher than that of metallic conductors.

We have so found five classes of conductors—metallic conductors, electrolytic conductors, insulators, arc conduction, and Geissler tube conduction. Unfortunately, here we find the same as in most phenomena of nature; as long as our knowledge is limited, we are able to subdivide in what appears distinct classes, but with the increasing amount of data, we find more and more cases which cannot well be grouped under one class or the other, but take an intermediate position between several classes. First, we usually try to overlook these intermediaries, as not fitting into our established classification, but ultimately we are forced to realize that what we had considered as distinct classes of phenomena are merely characteristic types, and that no dividing line exists, but a continuous transition by intermediary links from one type to another. These members, which stand intermediary between different types, are of special interest to science, in that usually a study of such intermediary types offers the best hope of reaching an insight into the nature of the phenomena.

So also we find intermediaries between the different classes, or rather types of conductors, and a number of such I desire to discuss.

Extremely interesting, also by reason of its commercial importance, is carbon. If we restrict our consideration to that carbon which has been maintained for a considerable time at arc temperature, that is, at the boiling point of carbon, and so is chemically pure, we find two allotropic modifications:

1. Amorphous carbon, characterized by a relatively high resistance, and negative temperature coefficient of resistance, so that at ordinary temperatures the resistance is nearly twice as high as at the melting point of platinum. The base of the incandescent lamp filament consists of this form of carbon.

2. Metallic carbon, characterized physically by metallic properties as high elasticity, metallic luster, etc., and electrically by a relatively low resistance, approaching that of metallic conductors, and a positive temperature coefficient of about 0.1 per cent. per degree C.—that is, the same magnitude as that of mercury or cast iron, so that the resistance of metallic carbon at the melting point of platinum is more than twice as high as at ordinary temperature. The coating of the "Gem" filament incandescent lamp consists of this form of carbon.

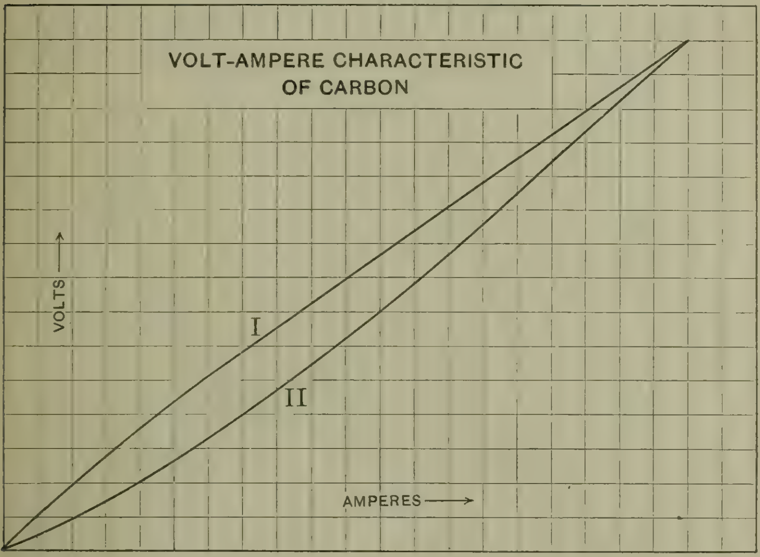

FIG. 7.

Volt-ampere characteristics of these modifications of carbon are shown in Fig. 7, and the resistance-temperature characteristics in Fig. 8. The latter are calculated from the former by the radiation law, $W = cT^4$, assuming the temperature of the incandescent lamp filament at 3.1 W per horizontal candle, as

1,800° C. (An error in this temperature would not affect the shape of the curve.)

As seen, the resistance of metallic carbon at 20° C. is 480 microhm-centimeters, or less than five times that of cast-iron, while that of amorphous carbon at 20° C. is 34,000 microhm-centimeters, or 0.04 ohm-centimeters—that is, nearly 100 times as high as that of metallic carbon, and already approaching the magnitude of electrolytic conduction.

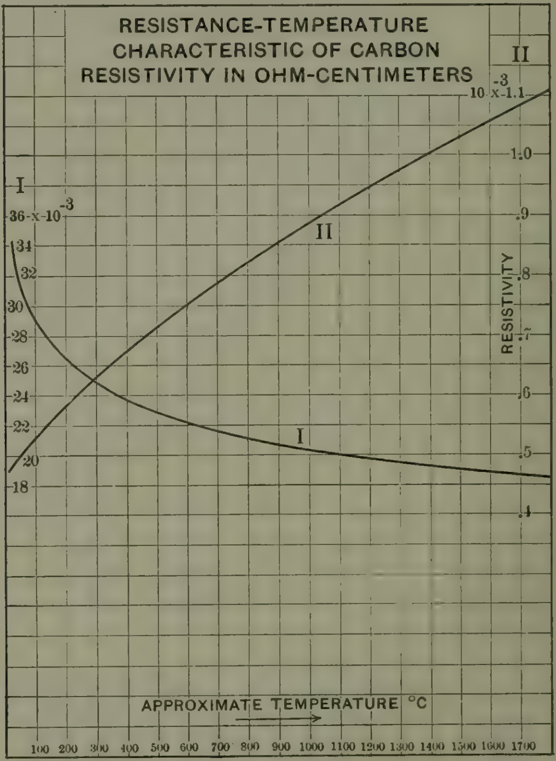

Fig. 8.

Curves Figs. 7 and 8 show that these two modifications of carbon imitate the resistance-temperature characteristic of metallic conductors and of electrolytic conductors, respectively, and the magnitude of their resistance is intermediate also between that of the two types of conductors. Carbon can therefore be said, to a certain extent, in its electrical characteristics, to bridge the gap between metallic and electrolytic conductors.

In some respects, silicon is possibly still more interesting. I have here some rods of cast silicon of 10-inch length and 0.22-inch diameter. The volt-ampere characteristics of two such rods are given in Fig. 9, the resistance temperature characteristic estimated from the radiation law in Fig. 10.

The difference between the two rods (a ratio of resistance of about 40 to 1, when cold, but nearly the same at very high temperature) is due to different amounts of foreign materials, probably carbon, dissolved in the silicon.

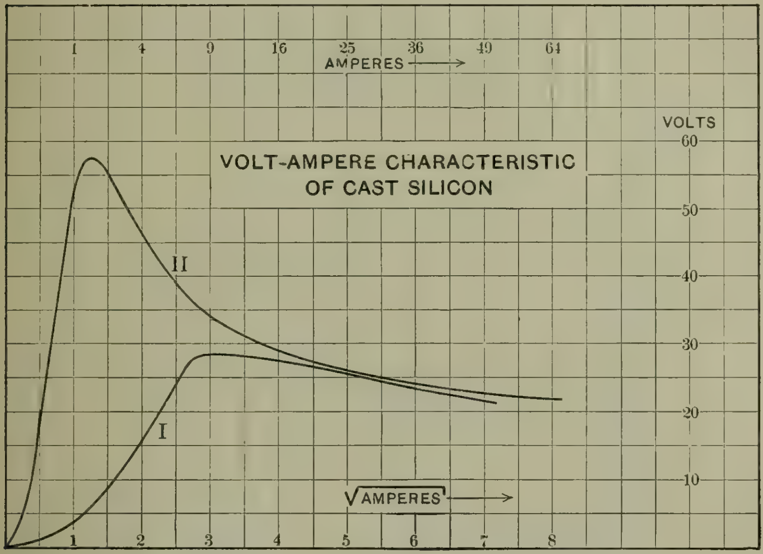

Fig. 9.

As seen, the resistance is practically constant up to a dull red heat; sometimes, as in rod I, it slightly rises up to a maximum at dull red heat, and then slightly decreases, up to a bright red heat. Above red heat, however, the resistance of cast-silicon falls, first very rapidly, then more slowly, but always falls at a greater rate than the increase of current required to give the temperature rise, so that from red heat upwards, the voltage consumed by a silicon resistance decreases with increase of current—that is, it exhibits the same electrical feature which is characteristic of arc conduction.

The volt-ampere curve of silicon rod I has, therefore, below red heat the characteristic of metallic conduction, at red heat the characteristic of electrolytic conduction, and from red heat up to the melting point, probably at 1,400° C., the characteristic of arc conduction. While, then, cast-silicon, by the absence of conversion of energy into any other form than heat, would have to be classed as metallic conductor, its electrical characteristics, throughout most of the temperature range, entirely differ from those of metallic conductors. It is, besides, not quite impossible that at high temperature silicon exhibits phenomena of luminescence—that is, transformation of some electrical

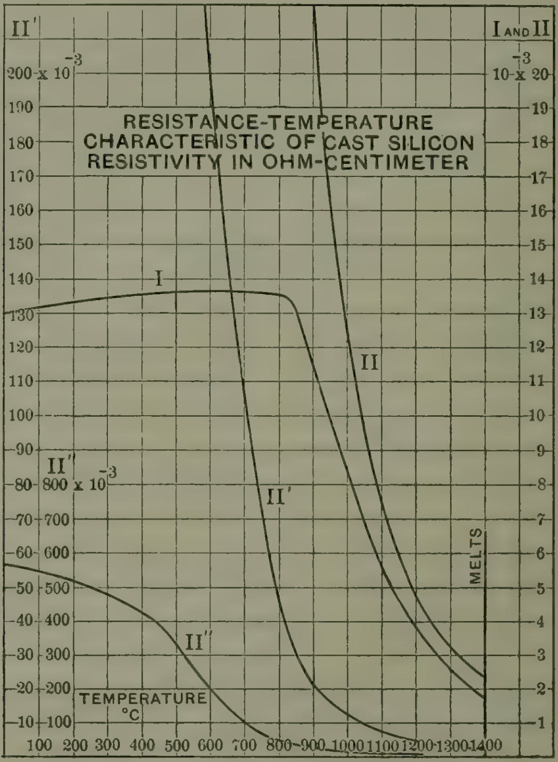

Fig. 10.

energy into light without heat as intermediary form of energy, and electroluminescence is a characteristic property of arc conduction and Geissler tube conduction.

The range of specific resistance of cast silicon, rod II, varies, as far as observed, between 0.56 ohm-centimeter at 20° C.—that is, the same magnitude as electrolytic conduction, down to 0.0024 ohm-centimeter near the melting point, and even very much lower values in other samples close to the range of metallic conduction.

This extremely high negative temperature coefficient of resistance, which gives the volt-ampere curve arc characteristics, is still more marked with a class of conductors of the constitution:

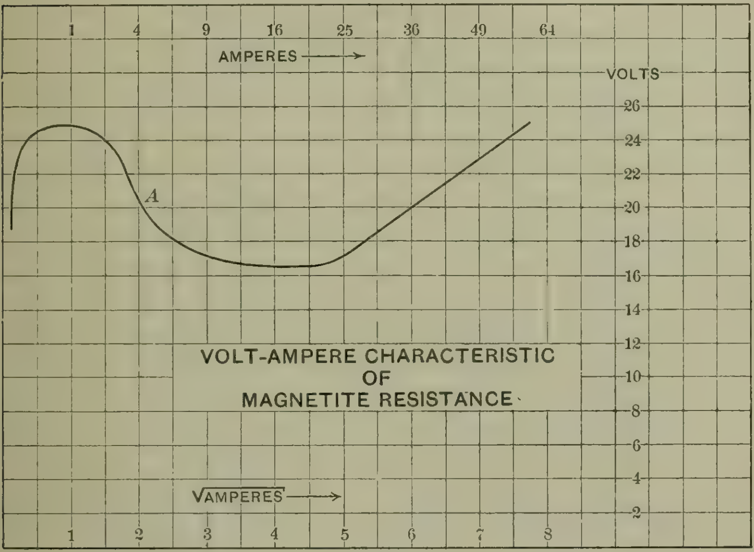

FIG. 11.

$$M^{(II)}\,M_2^{(III)}\,O_4$$

where $M^{(II)}$ is a bivalent metal, as Fe, Mn, Mg, Ca, $M^{(III)}$ is a trivalent metal, as Fe, Cr, Mn, or Al. One of these conductors, a so-called "magnetite resistance," I show you here. It is a mixture of magnetite with chromite—that is, $M^{(II)}$ is iron, $M^{(III)}$ is iron and chromium, the former preponderating. The rod has 6-inch length and ¾-inch diameter.

Its volt-ampere characteristic is given in Fig. 11, its resistance-temperature characteristic, as estimated from the radiation law, in Fig. 12. As seen, here the resistance-temperature characteristic shows very little of the electrical feature; at a certain moderate temperature, about 100° C., the resistance begins to decrease very rapidly, and falls to 1/650 of its initial value when approaching the melting point.

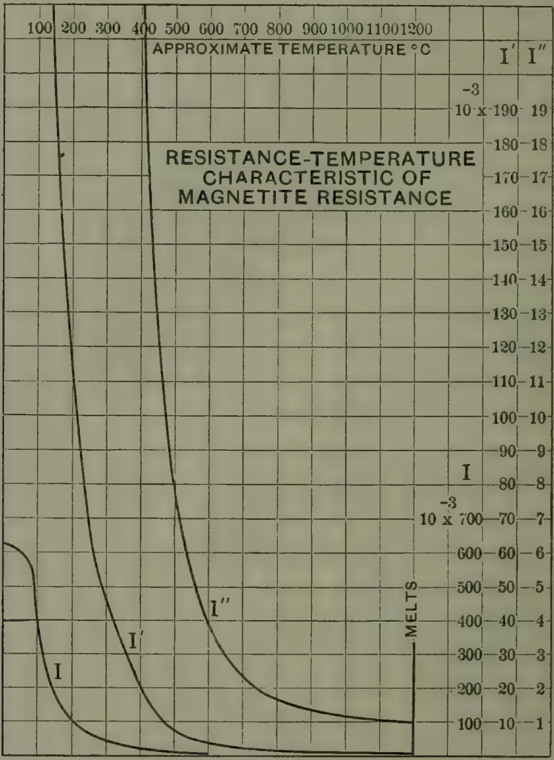

FIG. 12.

These resistances have the curious feature of a limiting voltage; in stationary condition, the potential drop across the resistance cannot exceed 25 volts, and with increasing current the voltage first rises, then reaches a maximum, and then decreases again, ultimately at very high temperature, to rise once more. Thus, with the same terminal voltage across the resistance, three different values of current can exist, as in the present case, at the terminal voltage of 20, the current may have either of the values of 0.02, 4.1, or 36 amperes. With constant impressed voltage, the second value is unstable, but requires a drooping characteristic of the electric circuit, just as an electric arc.

The volt-ampere characteristics frequently are plotted with $\sqrt{i}$ that is, the square root of the current, as abscissae, since this gives a better scale. This is, for instance, done in Figs. 6, 9 and 11.

As seen from Figs. 11 and 12, the volt-ampere characteristic of this material for low current is that of electrolytic conduction, for high currents that of arc conduction, and for very high currents again that of electrolytic conduction, and, indeed, ultimately the conductor becomes an electrolytic conductor and, after fusion, follows Faraday's law of conduction.

I have therefore called conductors of this type pyro-electrolytes.

It is interesting that in the range below fusion such conductors may carry very large direct currents, 20 to 30 amperes, and still no trace of chemical action occurs, although in the present case, at such high currents and with iron as expected deposit, no such explanation as a rediffusion of oxygen, which again consumes the deposited metal (as it has been assumed with the Nernst lamp glower to explain the absence of chemical dissociation), can possibly be attempted.

In most conductors of this class, the initial resistance, and so the voltage at the peak of the curve, is so high that the total curve cannot be experimentally observed as mere volt-ampere characteristic, since the voltage required to carry the current beyond the maximum voltage point is beyond the voltage which would shunt the conductor by a static spark. The complete curve could therefore only be determined by starting the conductor by artificial heat, and the use of a constant current supply.

In this class of conductors also belongs the glower of the Nernst lamp, and its range of operation is on the decreasing voltage curve, about A in Fig. 11, where the volt-ampere curve has an arc characteristic. The Nernst lamp glower on constant potential supply is, therefore, unstable, just as an arc, and requires for its operation a steadying resistance or reactance.

These pyro-electrolytes, therefore, take an intermediate position between the different types of other conductors, combining features of arc conduction, metallic conduction, and electrolytic conduction, indeed, changing from a conductor which has all the characteristics of metallic conduction, sometimes even a positive temperature coefficient, over a range of arc conduction into true electrolytic conduction, and may be represented as a type of their own.

Silicon, as illustrated in Figs. 9 and 10, then would give an intermediate link between pyro-electrolytic and metallic conduction.

A curious question arises here; some of these pyro-electrolytes change from the solid to the liquid state gradually—that is, through a viscous condition. As solids, even when incandescent, no chemical action accompanies their conduction, while when fused they follow Faraday's laws of electrolysis. There must then be a gradual transition from no chemical action to complete chemical action in the passage through the viscous state. It would be very interesting to investigate this state, where conductivity changes from metallic to electrolytic.

These investigations of the conductivity of metal oxides and other compounds also throw some light on the character of the so-called "insulators." It seems that what are commonly called insulators consist of two distinct classes:

1. Pyro-electrolytes, in which the initial resistance, or resistance at ordinary temperatures, is so high that practically no current passes, but which with increasing temperature decrease in resistance, so that at high temperature they become fairly good conductors, and ultimately, when approaching fusion or after fusion, chemical dissociation appears. Hereto belong, for instance, the silicates, as glass and mica, also most metallic oxides, as magnesia, etc.

2. Substances of very high resistance, usually with negative temperature coefficient of the resistance—that is, in which with increasing temperature the resistance decreases, but never so far that the conductivity reaches appreciable values. These are usually organic compounds, as rubber, fiber, etc., and chemical destruction limits their temperature. In these, the nature of the

conduction is still unknown, but it may possibly be accompanied by mechanical destruction or disintegration.

It almost seems advisable, therefore, to separate the classes of substances usually denoted as *insulators*, and put the first subdivision under the type of pyro-electrolytes.

We would then get the following types of conductors:

1. Metallic conductors.
2. Electrolytic conductors.
3. Pyro-electrolytes.
4. Insulators.
5. Arcs.
6. Geissler discharges.

To conclude, then, it seems that what has formerly been considered as different classes are merely types of conductors, between which numerous intermediates exist, and it is these intermediaries between different characteristic types which are of special interest, since it is in their study that a clearer understanding of the nature of electric conduction may at some time be reached.

APPENDIX.

To enable others to repeat the experiments conveniently, in the following the dimensional data of the apparatus are given:

In Fig. 3 (and 4) the transformer is of 1,500 watt, 60-cycle, with two low-tension coils wound for 115 volts, and two high-tension coils wound for 1,150 volts. It is connected series—multiple, as shown, to get a ratio 1 ÷ 20.

The reactances, x, x_1, x_0, have laminated iron cores of 2″ x 2″ section, and a nearly closed magnetic circuit, containing an air gap of 1/16″. The coil x is wound with 200 turns of wire No. 14, B. & S., giving an inductance of .04 henrys; the coils x_1 and x_0 are wound with 750 turns of wire No. 20, B. & S., giving an inductance of 0.6 henrys.

The condenser, K, is a 3,000-volt condenser (paraffined paper) of about 0.1 mf. capacity.

The A.C. voltage is varied by the field excitation; a constant alternating potential source of 220 to 250 volts, with a rheostat, can be used instead of A.C., Fig. 3, and, then, permits the connection of the condenser K to cd—that is, the operation of all three phenomena in the same tube.

The dimensions of the mercury tube are shown in Fig. 13, and separately, in the same figure, is shown one of the mercury cups. The tube diameter is 1″, the diameter of the mercury cup 1″ at the top, ½″ at the bottom. The leading-in wires are .040″ diameter, platinum, melted into heavy copper wire at the outside. To exhaust the tube, it is connected to a Boltwood mercury pump, by a mercury seal stopcock, to a funnel tube to let in the mercury, and by mercury seal stopcocks to an electrolytic hydrogen generator, with two P_2O_5 cups interposed, which are used as measuring flasks for the hydrogen. Glass spirals are interposed between tube and pump and between tube and hydrogen supply, to give flexibility, and all connections are made by welding the glass together, using no rubber tubing. The tube is exhausted, and heated, by a heating chamber or the Bunsen flame, to as near the softening point of glass as possible, until the vacuum is perfect; then, while hot, the tube is washed out several times with hydrogen at low pressure; then, after the vacuum is perfect, the mercury admitted very slowly, until the mercury cups are filled, the arc started from a to b, by tilting, with a as negative, shifted from b to c by increasing the resistance in anode b and decreasing it in anode c, and in the same manner shifted to d, running the arc at about 8 amperes. When no more

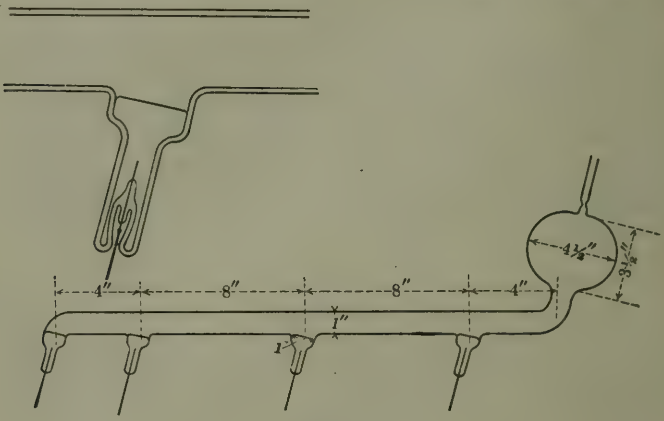

FIG. 13.

gas is given off, but the pump shows a perfect vacuum, the circuit is opened, some hydrogen is again admitted and exhausted, the arc started from a to b as soon as during exhaustion it holds, and the exhaustion continued until the arc, at 4 amperes, nearly fills the whole tube. Then the tube is sealed off.

In the calculation of the temperature-resistance characteristics of carbon from the volt-ampere characteristics, the assumption has been made that at a luminous efficiency of 3.88 watts per mean spherical candle-power (corresponding to 3.1 watts per mean horizontal candle-power) the temperature of the carbon is 1,800° C. If this temperature is not correct, a change of it would merely shift the abscissae of Fig. 8 proportionally.

The same applies to Figs. 10 and 12, the temperature resistance characteristics of silicon and magnetite, which are calculated upon the assumption that the melting point of silicon is 1,400° C., the melting point of the magnetite resistance 1,200° C. The general character of the curves, and the conclusions therefrom, are in no way affected by the uncertainty of the temperature assumption, but merely the numerical values of temperature changed.

The silicon resistances, Figs. 9 and 10, give the average analysis: Al, 0.04%; Ca, 0.35%; Fe, 0.35%; Mg, 0.03%; Mn, 0.04%; Zn, 0.10%; C, 1.4 to 0.10%.

The higher value of carbon corresponds to the lower resistance.

The magnetite resistance, Figs. 11 and 12, had the composition: Fe_3O_4, 90%; $FeCr_2O_4$, 9%; Na_2SiO_3, 1%.

DISCUSSION.

DR. C. A. DOREMUS: Tyndall, of London, has said that "As science progresses, definitions become blurred." Dr. Steinmetz has given us a practical illustration. It shows how impossible it is to classify with sharp lines of demarcation between these different forms of conductors. I am sure I express for each and every one of the audience their sense of a great debt of gratitude to Dr. Steinmetz for having made so simple and so clear a fund of experimental knowledge and theoretical consideration, which probably no man except Dr. Steinmetz possesses.

A discussion held at the Eleventh General Meeting of the American Electrochemical Society, in Philadelphia, Pa., May 2, 1907; President Carl Hering in the chair.

RECENT IMPROVEMENTS IN ELECTROCHEMICAL ANALYSIS.

A DISCUSSION, OPENED BY DR. EDGAR F. SMITH.

DR. E. F. SMITH *(remarks condensed):* In 1880, Dr. Wolcott Gibbs, before the National Academy of Science, used a cathode of mercury for receiving a metal precipitated electrolytically from solution, and by the increased weight of the mercury determined the amount of metal precipitated. Again in 1883, before the same academy, he alluded to this scheme, but did not furnish any experimental data.

A few years ago we modified the apparatus somewhat, carrying out Dr. Gibbs' idea in a large test tube, flattened out at the bottom, with a platinum wire sealed through the bottom to connect with the mercury. By rotating the anode, large quantities of copper can be deposited in a short time; an analysis of copper sulphate can be made in ten minutes. Zinc in zinc sulphate is similarly determined; also sulphates of iron, cobalt, nickel and cadmium. Iron is thus easily separated from titanium, zirconium, uranium, sodium, cerium, lanthanum and thorium.

If sodium only is in solution it enters the mercury, while chlorine, iodine or bromine may be caught on a silver anode and weighed directly. The sodium is removed afterwards from the mercury by water, and titrated as caustic soda. If it is not desired to collect the chlorine, a thin layer of toluene is placed upon the solution and an unattackable anode is used; the chlorine then attacks the toluene and disappears.

Dr. Smith showed a small apparatus for the alkali determination which was a miniature reproduction of the Castner mercury cell, and explained its uses for electrolytic quantitative analysis. Using proper voltage, barium is thus separated from calcium and magnesium; by raising the voltage, calcium is afterwards separated from magnesium, the latter remaining inside as hydrate. If a fluoride solution is electrolyzed, the fluorine can be caught on an anode of zinc or lead, but also by calcium hydrate on a platinum gauze anode, forming calcium fluoride on the wire. Using sodium fluoride solution of known strength, a pulverized silicate can be suspended in the electrolyte, and is decomposed by the fluorine at the anode, its alkaline base going into the amalgam and being there determined. Silicates are thus broken up as easily as chlorides or sulphates. We wish to analyze feldspar, thus determining almost at one stroke its alkalies, silica and alumina. Anyone who wishes can see the processes I have described in operation in our electrolytic room on the north side of this laboratory.

Dr. W. D. Bancroft: I am sorry that Dr. Smith still feels it necessary to classify himself as "only a chemist," but I think the Society can rejoice in the fact that he is a very first-class chemist, and that it is not any exaggeration at all to say that practically all the recent improvements in electrolytic analysis have come from the John Harrison Laboratory, here at the University of Pennsylvania. I was especially interested in seeing that the Castner process for making caustic soda and chlorine commercially has now been modified so as to give us a method of quantitative analysis.

Prof. Chas. F. Chandler: Dr. Smith's story is a novel, and is the most interesting chemical paper I have ever listened to. Being myself "only a chemist," there was one thing he said which troubles me, and perhaps some electrician may set me right. I have always understood that ions laden with electricity were muzzled, and could not do any chemical work until they reached the electrode and discharged their characteristic electricity. Now Dr. Smith tells us that when he puts his pebbles of feldspar into the liquid, that the fluorine ions immediately attack it and disintegrate it. I really should like to have that little doubt in my mind cleared up by some electrician.

President Hering: Will someone volunteer? I guess we will have to call on Dr. Bancroft.

Dr. Bancroft: I think it had better be explained by the man who did it.

Dr. Smith: All I know is that the alkali in the feldspar gets into such a shape that it comes outside the mercury, and there is determined. I don't see what else could act upon the feldspar if it were not the fluorine in solution, from the sodium fluoride. I don't know anything more about it, except that we can measure it on the outside.

Dr. William H. Walker: Without wishing to disparage in the least the value of Prof. Smith's splendid paper, and while I do not attempt to answer Prof. Chandler's very pertinent questions, it may throw some light upon the matter to mention the work of Dr. Allerton S. Cushman, of the Office of Public Roads, Washington, in the matter of the decomposition of feldspar by the electric current. Dr. Cushman observed that the hydrolysis, which feldspar suffers when mixed with water, ceases when the concentration of alkali set free is yet small. If, however, the suspended finely-ground feldspar be subjected to electrolysis, the potash is found to move quite rapidly toward the cathode, while the anode chamber becomes acidic in reaction. While the presence of a small amount of hydrofluoric acid greatly accelerates the action, a very material decomposition can be brought about without the presence of any foreign electrolyte. Dr. Cushman's decomposition was not, however, complete, and could not be used as an analytical method in the sense of the process described by Prof. Smith.

Dr. H. E. Patten: I would like, in this connection, to suggest that the same method is given in Bulletin No. 30 of the Bureau of Soils, of the United States Department of Agriculture, by F. K. Cameron and James M. Bell.

Dr. Smith: This method?

Dr. Patten: Yes.

Dr. Smith: The use of sodium fluoride?

Dr. Patten: No, the one just referred to.

Dr. Smith: In Mr. Cushman's decomposition of the feldspar, he uses hours and high currents. This is done in an hour, and with low current—not over 3½ volts.

Dr. Walker: I was not wishing to disparage the value of this process at all.

Dr. Smith: I saw the paper; I have it in my office. My process occupies an hour's time, whereas Dr. Cushman's takes days, I believe. I was very careful not to read his paper, after I saw the title, until after we had made these determinations.

Dr. Patten: My remark was in no sense directed to this paper of Dr. Smith, as given, but it is simply a question of priority in the matter of the work with regard to this electrolysis of feldspar which has arisen, and in this connection that paper ought to be mentioned.

Dr. Doremus: You can get alkali from the feldspar by the repeated treatment with water to a considerable extent, and the experiments of Cushman show this is aided by electrolysis, and passes out of a cell by endosmose. There may be a great many chemical reactions occurring simultaneously in which the fluorine takes part, and I would like to ask Dr. Smith whether he tried either magnesium or copper as an anode in the fluorine experiment.

Dr. Smith: Copper.

Dr. Doremus: Did you try magnesium?

Dr. Smith: No. I think we have some magnesium with the calcium hydrate.

I am very glad that Dr. Walker called attention to Dr. Cushman's paper, because it is certainly a most important paper, and so far as priority is concerned, it doesn't matter to me; I hope somebody else has noticed this long before. The desire I have is to analyze a silicate completely, if possible, by the help of the electric current, and that is our contribution towards it. If Prof. Cushman can help us along or make use of it, make use of anything, we will give him all the credit. That is the only desire we have—to decompose, if possible, the silicate, and determine every component of it in the electrolytic way. The time factor, of course, is important. In the old days of electro-analysis, the determination of metals in that fashion was tedious, because it took all night. Then those of us who were interested, labored long and hard, and got it down to hours and minutes. And if you press us, we will get it to moments; so it is in this work we are aiming at time, as well, and whether we will succeed with feldspar and other silicates or not, I cannot say now; but we trust we shall succeed, and in doing this work, too, within a period that will appeal to the analyst. I think the fluorine is doing something there—that is, helping cut down that time factor very materially.

PRESIDENT HERING: In the analysis of sulphates, if an anode of a spongy lead is used, it will get rid of the sulphuric acid which is formed, and is sometimes a hindrance in getting out the rest of the metal, as with zinc sulphate, for instance. I have gotten good results with the use of ordinary negative storage battery plate, used as an anode, for combining with the sulphuric acid formed in the electrolysis of zinc sulphate.

A paper read by Prof. W. D. Bancroft at the Eleventh General Meeting of the American Electrochemical Society, in Philadelphia, Pa., May 3, 1907; President Hering in the chair.

ELECTRODEPOSITION OF ZINC.

BY RALPH C. SNOWDON.

In the spring of 1904, I made a preliminary examination of some of the conditions affecting the electrodeposition of zinc. I have not been able to take the question up more carefully, and I have therefore decided to publish the data, as they bring out some points which are not matters of common knowledge. The variables taken into account were: concentration, degree of acidity and alkalinity, reducing agent, current density, and temperature. While the cathode was rotated in every case, no attempt was made to measure the rate of rotation carefully or to keep it constant. It was thought that differences in speed would be of minor importance, provided a fairly high rate of speed was maintained. The results of the experiments have proved that this was a delusion. It is scarcely overstating the matter to say that the limiting current density at which the deposit begins to become bad depends more on the rate of stirring than on all the other factors combined.

In Table I are given the solutions which were studied.

TABLE I.

Sol.	Composition
A	$M/2\ ZnSO_4 + M/50\ H_2SO_4$.
B	$M/2\ ZnSO_4 + M/5\ H_2SO_4$.
C	$M/2\ ZnSO_4 + M/50\ H_2SO_4 + M/10$ resorcinol.
D	$M/10\ ZnSO_4 + M/50\ H_2SO_4$.
E	$M/10\ ZnSO_4 + M/5\ H_2SO_4$.
F	$M/10\ ZnSO_4 + M/50\ H_2SO_4 + M/10$ resorcinol.
G	Saturated solution of ZnO_2H_2 in 3M NaOH.
H	Add 60g. solid NaOH (3M/2) per liter of Solution G.
I	Add 11g. resorcinol (M/10) per liter of Solution G.
K	Dilute solution G to one-fourth with 3M NaOH.
L	Add 60g. solid NaOH (3M/2) per liter of Solution K.
M	Add 11g. resorcinol (3M/2) per liter of Solution K.

Measurements were made with each solution at 20°, 40° and 70°, using a large sheet-iron water-bath, heated by Bunsen burners. In this bath a given temperature could be kept to within 2°-3° of the temperature desired. This bath would accommodate four solutions at one time and so the runs were made in sets of four each. The solutions were contained in 500 cc. beakers, each cell having two zinc anodes, with a rotating cathode placed between them. The cathodes were zinc tubes, one centimeter in diameter and dipped full five centimeters into the solution, making a total cathode surface of a trifle over 16 square centimeters. Each cathode was turned by an individual motor making 200-300 revolutions per minute. The current and voltages were all taken on the specially brightened surface of the connector which held the rotating cathode fast to the shaft of the motor. In each particular case the readings were quite constant; but that, of course, does not mean that they were free from error. An imperfect contact between the voltmeter and the rotating cathode, an imperfect contact between the rotating connector and the rotating cathode, or a slight fluctuation in the temperature would all introduce quite serious errors. While it is hoped and believed that errors due to these causes were small, the measurement of the voltages was a secondary matter, and it would not be safe to base conclusions on minor fluctuations in the voltages. The polarization voltages were not determined in any case.

By means of a sliding resistance, current densities were varied in steps of 0.5 amperes usually up to 7 amp/dm². After that the current density was increased rapidly up to the values at which the deposits became hopeless.

In Tables II-X are given all the data except the limiting current densities, these last being put all together in Table XI.

TABLE II.

TEMP. 20°

Sol.	Amp./dm²	Volts	Remarks	Sol.	Amp./dm²	Volts	Remarks
A	1.0	0.55	All deposits granular and spiral.	A	1.5	0.91	All deposits granular but spreading.
B	1.0	0.32		B	1.5	0.41	
C	1.0	0.41		C	1.5	0.55	
D	1.0	0.48		D	1.5	1.23	
A	2.0	0.97	Deposits granular but becoming smoother.	A	2.5	1.34	Same as preceding but C smoother.
B	2.0	0.54		B	2.5	0.86	
C	2.0	0.73		C	2.5	1.10	
D	2.0	1.90		D	2.5	2.82	
A	3.0	1.65	All deposits smoother.	A	3.5	1.70	Deposits still granular but very metallic looking.
B	3.0	0.97		B	3.5	1.10	
C	3.0	1.55		C	3.5	1.65	
D	3.0	3.10		D	3.5	3.20	
A	4.0	1.90	All deposits stronger and smoother.	A	4.5	2.00	No change in deposits.
B	4.0	1.40		B	4.5	1.50	
C	4.0	1.90		C	4.5	2.10	
D	4.0	3.60		D	4.5	4.00	
A	5.5	2.15	A, B and C good; D poor.	A	6.0	2.65	Same as in preceding run.
B	5.5	1.60		B	6.0	1.70	
C	5.5	2.00		C	6.0	2.40	
D	5.5	4.00		D	6.0	4.50	
A	6.5	2.90	A, B and C good; D bad.	A	7.0	3.00	All deposits fair.
B	6.5	2.15		B	7.0	2.20	
C	6.5	2.50		C	7.0	2.65	
D	6.5	4.30					
A	7.5	3.20	All deposits fair.	A	8.0	3.30	All treeing.
B	7.5	2.20		B	8.0	2.50	
C	7.5	2.80		C	8.0	3.30	
C	8.5	3.50	Only fair.	C	9.0	3.50	Poor and non-adherent.

TABLE III.

TEMP. 40°

Sol.	$\frac{\text{Amp.}}{\text{dm}^2}$	Volts	Remarks	Sol.	$\frac{\text{Amp.}}{\text{dm}^2}$	Volts	Remarks
A	0.5	0.50	No precipitate on B; rest granular. Not very adherent.	A	1.0	0.39	Becoming finely granular and more adherent.
B	0.5	0.15		B	1.0	0.30	
C	0.5	0.35		C	1.0	0.46	
D	0.5	0.30		D	1.0	0.36	
A	1.5	0.54	All deposits finely crystalline and adherent. D very hard and fine.	A	2.0	0.77	All good and adherent, somewhat spiral. A poorest, D best.
B	1.5	0.36		B	2.0	0.41	
C	1.5	0.57		C	2.0	0.78	
D	1.5	0.53		D	2.0	0.96	
A	2.5	0.96	All deposits good; A especially smooth though not bright.	A	3.0	0.93	All deposits fine.
B	2.5	0.60		B	3.0	0.36	
C	2.5	0.87		C	3.0	0.98	
D	2.5	1.46		D	3.0	1.60	
A	3.5	1.00	A, B, C fine. B a bit too granular. All adherent.	A	4.0	1.20	All deposits fine.
B	3.5	0.35		B	4.0	0.40	
C	3.5	1.30		C	4.0	1.25	
D	3.5	1.80		D	4.0	2.10	
A	4.5	1.30	All deposits fine.	A	5.0	1.50	A, C, D fine. B slightly spotted but adherent.
B	4.5	0.60		B	5.0	0.90	
C	4.5	1.40		C	5.0	1.60	
D	4.5	2.10		D	5.0	2.50	
A	5.5	1.60	A, C, D good. B hard and spotted.	A	6.0	1.90	A, C, D good. B hard and spotted.
B	5.5	1.00		B	6.0	1.10	
C	5.5	1.90		C	6.0	2.00	
D	5.5	2.90		D	6.0	3.10	
A	15.0	4.00	All deposits good.	A	16.0	4.10	A, B, C good. D poor.
B	15.0	2.60		B	16.0	2.80	
C	15.0	4.70		C	16.0	4.90	
D	15.0	6.50		D	16.0	7.40	

TABLE IV.

TEMP. 70°

Sol.	$\frac{\text{Amp}}{\text{dm}^2}$	Volts	Remarks	Sol.	$\frac{\text{Amp.}}{\text{dm}^2}$	Volts	Remarks
A	0.5	0.30	All deposits consist of large separate crystals.	A	1.0	0.33	All deposits crystalline and adherent. D best.
B	0.5	0.15		B	1.0	0.16	
C	0.5	0.30		C	1.0	0.28	
D	0.5	0.20		D	1.0	0.36	
A	1.5	0.39	All deposits crystalline and adherent.	A	2.0	0.51	Same as preceding.
B	1.5	0.20		B	2.0	0.25	
C	1.5	0.45		C	2.0	0.55	
D	1.5	0.44		D	2.0	0.60	
A	2.5	0.72	Same as preceding.	A	3.0	1.10	Same as preceding.
B	2.5	0.26		B	3.0	0.30	
C	2.5	0.65		C	3.0	0.69	
D	2.5	0.70		D	3.0	0.79	
A	3.5	1.32	Same as preceding.	A	4.0	1.20	All deposits adherent, C most so All crystalline, D least so.
B	3.5	0.35		B	4.0	0.44	
C	3.5	0.78		C	4.0	0.86	
D	3.5	1.10		D	4.0	1.30	

TABLE V.

TEMP. 20°

Sol.	$\frac{\text{Amp.}}{\text{dm}^2}$	Volts	Remarks	Sol.	$\frac{\text{Amp}}{\text{dm}^2}$	Volts	Remarks
E	0.5	0.35	Crystalline and non-adherent.	E	1.0	0.37	E, G, H good and adherent; F crystalline and non-adherent
F	0.5	0.40		F	1.0	0.55	
G	0.5	0.10		G	1.0	0.28	
H	0.5	0.18		H	1.0	0.32	
E	1.5	0.40	All good, E and F the better.	E	2.0	0.52	All good.
F	1.5	0.68		F	2.0	0.90	
G	1.5	0.18		G	2.0	0.38	
H	1.5	0.33		H	2.0	0.35	
E	2.5	0.52	All good, G and H smooth and adherent.	E	3.0	0.56	E fair, F crystalline, G and H good.
F	2.5	1.05		F	3.0	1.32	
G	2.5	0.29		G	3.0	0.36	
H	2.5	0.39		H	3.0	0.42	
E	4.0	0.78	F, G, H good, E fair.				
F	4.0	1.80					
G	4.0	0.44					
H	4.0	0.47					

TABLE VI.

TEMP. 40°

Sol.	Amp. / dm²	Volts	Remarks	Sol.	Amp. / dm²	Volts	Remarks
E	0.5	0.30	All deposits fair and crystalline.	E	1.0	0.42	F and G good, E and H fair.
F	0.5	0.41		F	1.0	0.56	
G	0.5	0.04		G	1.0	0.06	
H	0.5	0.07		H	1.0	0.09	
E	1.5	0.60	All deposits good.	E	2.0	0.63	All deposits good.
F	1.5	0.80		F	2.0	1.04	
G	1.5	0.06		G	2.0	0.07	
H	1.5	0.09		H	2.0	0.12	
E	2.5	0.76	All deposits good.	E	3.0	0.90	All deposits good.
F	2.5	1.33		F	3.0	1.70	
G	2.5	0.09		G	3.0	0.11	
H	2.5	0.14		H	3.0	0.19	
E	3.5	1.00	All deposits good.	E	4.0	1.12	All deposits good.
F	3.5	1.90		F	4.0	2.00	
G	3.5	0.12		G	4.0	0.13	
H	3.5	0.26		H	4.0	0.28	

TABLE VII.

TEMP. 70°

Sol.	Amp. / dm²	Volts	Remarks	Sol.	Amp / dm²	Volts	Remarks
E	0.5	0.13	E and H good. F and G non-adherent.	E	1.0	0.20	Same as preceding.
F	0.5	0.23		F	1.0	0.30	
G	0.5	0.02		G	1.0	0.03	
H	0.5	0.02		H	1.0	0.03	
E	1.5	0.29	Same as preceding.	E	2.0	0.36	Same as preceding.
F	1.5	0.53		F	2.0	0.75	
G	1.5	0.04		G	2.0	0.05	
H	1.5	0.04		H	2.0	0.04	
E	2.5	0.43	All deposits good.	E	3.0	0.53	All deposits good.
F	2.5	0.92		F	3.0	1.13	
G	2.5	0.06		G	3.0	0.06	
H	2.5	0.05		H	3.0	0.05	
E	3.5	0.65	All deposits good.	E	4.0	0.75	E, F and G good. H poor.
F	3.5	1.26		F	4.0	1.55	
G	3.5	0.07		G	4.0	0.08	
H	3.5	0.06		H	4.0	0.07	

TABLE VIII.

TEMP 20°

Sol.	$\frac{\text{Amp.}}{\text{dm}^2}$	Volts	Remarks	Sol.	$\frac{\text{Amp.}}{\text{dm}^2}$	Volts	Remarks
I	0.5	0.05	All deposits light but good.	I	1.0	0.06	I, K, and L good. M fair.
K	0.5	0.05		K	1.0	0.07	
L	0.5	0.08		L	1.0	0.07	
M	0.5	0.05		M	1.0	0.07	
I	1.5	0.08	I, K and L good. M fair.	I	2.0	0.09	All deposits good.
K	1.5	0.08		K	2.0	0.09	
L	1.5	0.08		L	2.0	0.09	
M	1.5	0.08		M	2.0	0.09	
I	2.5	0.10	All deposits good.	I	3.0	0.12	All deposits good.
K	2.5	0.11		K	3.0	0.12	
L	2.5	0.10		L	3.0	0.12	
M	2.5	0.10		M	3.0	0.12	
I	3.5	0.14	All deposits good.	I	4.0	0.15	I good, K very fair, L fine, smooth and adherent. M only fair.
K	3.5	0.14		K	4.0	0.16	
L	3.5	0.14		L	4.0	0.16	
M	3.5	0.14		M	4.0	0.15	

TABLE IX.

TEMP. 40°

Sol.	$\frac{\text{Amp.}}{\text{dm}^2}$	Volts	Remarks	Sol.	$\frac{\text{Amp.}}{\text{dm}^2}$	Volts	Remarks
I	0.5	0.04	I, K and L good. M fair.	I	1.0	0.05	All deposits good.
K	0.5	0.04		K	1.0	0.05	
L	0.5	0.04		L	1.0	0.05	
M	0.5	0.05		M	1.0	0.06	
I	1.5	0.06	All deposits good.	I	2.0	0.08	All deposits good.
K	1.5	0.07		K	2.0	0.08	
L	1.5	0.06		L	2.0	0.08	
M	1.5	0.07		M	2.0	0.08	
I	2.5	0.09	All deposits good.	I	3.0	0.10	All deposits good.
K	2.5	0.09		K	3.0	0.10	
L	2.5	0.09		L	3.0	0.11	
M	2.5	0.09		M	3.0	0.10	
I	3.5	0.12	All deposits good.	I	4.0	0.13	I, K and L good, M fair. M good zinc but thin.
K	3.5	0.13		K	4.0	0.14	
L	3.5	0.12		L	4.0	0.13	
M	3.5	0.11		M	4.0	0.14	

TABLE X.

TEMP. 70°

Sol.	Amp. / dm²	Volts	Remarks	Sol.	Amp. / dm²	Volts	Remarks
I	0.5	0.03	I thin and fair, K good. L fair, M good.	I	1.0	0.03	K, L and M good, I very poor.
K	0.5	0.03		K	1.0	0.04	
L	0.5	0.03		L	1.0	0.04	
M	0.5	0.04		M	1.0	0.05	
I	1.5	0.04	Same as preceding.	I	2.0	0.05	Same as preceding.
K	1.5	0.05		K	2.0	0.05	
L	1.5	0.05		L	2.0	0.05	
M	1.5	0.06		M	2.0	0.06	
I	2.5	0.05	Same as preceding.	I	3.0	0.06	Same as preceding.
K	2.5	0.07		K	3.0	0.08	
L	2.5	0.06		L	3.0	0.07	
M	2.5	0.07		M	3.0	0.08	
I	3.5	0.07	Same as preceding.	I	4.0	0.08	Same as preceding.
K	3.5	0.09		K	4.0	0.10	
L	3.5	0.07		L	4.0	0.09	
M	3.5	0.08		M	4.0	0.10	

TABLE XI.

Current densities at which deposits go bad.

	TEMP. 20°		TEMP. 40°		TEMP. 70°	
Sol.	Amp. / dm²	Volts	Amp. / dm²	Volts	Amp. / dm²	Volts
A	8.0[1]	3.30	46.5	12.0	59.0	7.2
B	8.0[1]	2.50	49.5	9.9	55.8	4.5
C	8.0[1]	3.30	50.2	12.0	65.0	6.0
D	5.5[1]	4.00	31.0	11.6	43.5	9.4
E	34.0	6.0	28.0	5.0	28.0	3.9
F	34.0	15.3	18.6	6.1	15.2	4.6
G	18.6	1.7	54.0[2]	1.45	48.0[2]	0.8
H	15.5	0.9	18.2	0.7	4.0	0.07
I	18.6		18.6	0.48	1.0	0.03
K	12.4		9.3	0.30	15.2	0.30
L	12.4		9.3	0.25	9.3	0.15
M	15.2		12.4	0.35	21.7	0.35

[1] Run at slower speed than the others.

[2] Run at higher speed than the others.

In the runs with solutions A, B, C and D at 20° the immersed portion of the cathode was twice what it was in the later runs, and the motor gave a lower speed. The limiting values in Table XI are not comparable, therefore, with the corresponding values at 40° and 70°. To show that this difference is due to rate of stirring, a couple of runs were made on February 16, 1907, with solution A and another motor. By varying the speed of the motor, the current density at which the deposit became bad could be varied at will. With the highest speed, about 1,200 R. P. M., treeing began at the lower edges of the cathode when the current density was 60-65 amp/dm^2. Even at these values there were no signs of spongy zinc and the deposit was excellent over the bulk of the cathode surface. The limiting values for solution G at 40° and at 70° were obtained on a special run made in 1906. These enormous fluctuations, which were entirely unforeseen when the work was planned, make the actual figures for the current densities of practically no value so far as comparisons are concerned. They are valuable in showing what high current densities may be used, both in acid and alkaline solutions, provided precautions are taken to prevent impoverishment at the surface of the cathode. In fact, there is really no evidence that there would be any upper limit, in most cases, if one could prevent all impoverishment at the cathode surface. On the other hand, it must be remembered that the danger from treeing increases rapidly with increasing fall of potential through the electrolyte.

In general, the alkaline solutions begin to give bad results at a lower current density than the acid solutions. Against this we must set the facts that the deposits from alkaline solutions are smoother than those from the acid solutions, that the current efficiency is apparently higher, and that the voltage across the terminals is very low. This last is because zinc will precipitate readily from a strongly alkaline solution, while it does not come out so readily from strongly acid solutions. The presence of resorcinol seems to have very little effect one way or the other.

A few runs on current efficiency were made. The solutions selected were C at 70°, G at 70°, I at 40°, and a plating solution at 20°. The plating solution had the composition: $ZnSO_4 . 7H_2O$, 82.7g.; $(NH_4)_2 SO_4$, 22.6g.; water, 500 cc. Stationary cathodes were used, consisting of thin copper plates carefully cleaned. The solutions were run in series with a copper coulometer. With a current density of 1.5 amp/dm², the deposits from solutions G and I soon became so bad as to be unweighable. The following results were obtained with solution C at 70°, and with the plating solution at 20°, in a run lasting sixty-four minutes:

TABLE XII.

Solution	Current density	Deposit	% Efficiency
C at 70°	1.5 amp/dm²	1.670 g.	89.3
Plater at 20°	1.5 amp/dm²	1.845 g.	98.7

The deposit from the plating solution was much better than that from solution C; but both solutions showed signs of severe impoverishment around the cathode. The deposits were streaked and porous, that from solution C being decidedly granular. One run was made with alkaline solutions G and I at the much lower current density of 0.5 amp/dm², the run lasting thirty minutes. An apparent efficiency of 105.0 per cent. was obtained for G, and of 104.5 per cent. for I. This false efficiency is due to the impossibility of drying the spongy precipitates without causing oxidation, which would give an increased weight. This illustrates very clearly the effect due to stirring. With a rotating cathode, the current densities could have been increased enormously without causing the deposits to become bad. On account of the erroneous results which were originally obtained, certain experiments have been tried lately to re-determine the current efficiency in alkaline solutions[1] and to test the effect of a rapidly rotating cathode upon the quality of the deposit. For this purpose, Solution G was employed as the electrolyte and the cathode was rotated at a rate of 1,200 to 1,800 R. P. M., such speed being used as would favor the deposition of good adherent metal. The apparatus was practically the same as that used in making the original volt-ampere runs, with the addition of a copper coulometer. The numerical results are given in Table XIII:

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[1] February, 1907.

TABLE XIII.

Solution	Volts	Current density	Time	Deposit	% Efficiency
G at 20°	0.13	3.2 amp/dm²	40 min.	0.394 g.	99.49
G at 20°	0.6	20.0 amp/dm²	15 min.	0.930 g.	100.70

The zinc obtained with a current density of 3.2 amp/dm² was most excellent in quality, there being only a slight roughening on the cathode at the surface of the electrolyte. The zinc deposited at the higher current density appeared as rounded granules of the metal adhering slightly to a very finely crystalline under deposit. These runs also show the extremely low voltage at which zinc is precipitated from its alkaline solutions.

In the experiments previously described, the deposits were not saved, as it was necessary to use the cathodes over and over again. A few subsequent runs were made for the special purpose of studying the quality of the deposit under the microscope. The cathodes were copper plates 5 x 15 cm., immersed to a depth of 10 cm. in the solutions. These plates received a thin coating of zinc from a cyanide plating solution, so that there might be no evolution of hydrogen due to local action between the zinc and the copper. This plating solution was made up as follows:

Dissolve 1 gram neutral $ZnSO_4 . 7H_2O$ to 20-30 cc. water. Add enough potassium cyanide solution to re-dissolve the precipitated zinc cyanide and dilute to 150 cc. solution per gram of hydrated zinc sulphate originally taken. Electrolyze at any temperature with a current density of 5.0 amp/dm².

To test the effect of varying conditions, the following runs were made:

EFFECT OF TEMPERATURE.

Solution A, 10 amp/dm², at 20°, 40°, 70°.
Solution A, 1 amp/dm², at 40°, 70°.

EFFECT OF CURRENT DENSITY.

Solution A, 1.0 amp/dm² and 10 amp/dm², at 70°.
Solution A, 1.0 amp/dm² and 10 amp/dm², at 40°.
Solution A + 20 cc. 40 o/o formaldehyde, 1.0 amp/dm² and 10 amp/dm² at 40°.

EFFECT OF CONCENTRATION.

Solutions A and D, 1.0 amp/dm², at 40°.

Solutions A and D, 10 amp/dm², at 40°.

Solutions G and K, 3.0 amp/dm², at 40°.

Solutions G + 20 cc. 40 o/o formaldehyde and K + 20 cc. 40 o/o formaldehyde, 3.0 amp/dm², at 40°.

EFFECT OF REDUCING AGENT[1].

Solutions A and A + 20 cc. 40 o/o formaldehyde, 1.0 amp/dm², at 40°.

Solutions A and A + 20 cc. 40 o/o formaldehyde, 10 amp/dm², at 40°.

Solutions G and G + 20 cc. 40 o/o formaldehyde, 3.0 amp/dm², at 40°.

Solutions K and K + 20 cc. 40 o/o formaldehyde, 3.0 amp/dm², at 40°.

The solutions were all stirred thoroughly to prevent the collection of bubbles on the surface of the cathode, the acid solutions by means of a swiftly-revolving test-tube brush, and the alkaline ones with a revolving zinc plate. Both methods were effective. One anode and one cathode were used and the solutions were contained in 500 cc. beakers. Zinc anodes and the prepared copper (practically zinc) cathodes were always used.

From these runs it could in general be said that an increase in concentration or in temperature causes an increase in crystal size, while an increase in current density has the opposite effect and decreases the size of the crystals. Formaldehyde makes the deposit nearly amorphous; from sodium zincate solutions we get a deposit which is very finely crystalline.

The general results of this paper may be summed up:

1. Good deposits of zinc may be obtained from acid or alkaline solutions, even at such high current densities as 60 amp/dm².
2. The rate of rotation of the cathode has an enormous effect on the upper limit of the current density.

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[1] Formaldehyde was used instead of resorcinol in these runs because there was less likelihood of any formation of a complex salt and because the decomposition products are cleaner.

3. Since zinc will precipitate readily from strongly alkaline solutions, the resistance of these solutions, and consequently the voltage across the terminals, can be made very low for any given current density.
4. A high current efficiency may be obtained in alkaline solutions.
5. More finely crystalline deposits are obtained from alkaline than from acid solutions.
6. Increasing temperature or concentration increases the size of the crystals.
7. Presence of formaldehyde decreases the size of the crystals.
8. Increasing the current density decreases the size of the crystals.

This investigation was suggested by Professor Bancroft and carried out under his supervision.

Cornell University.

DISCUSSION.

MR. SPERRY: I would like to ask Dr. Bancroft what he means by stirring vigorously? What order of velocity existed at the electrodes?

PROF. BANCROFT: Anywhere from 200 to 1,200 revolutions per minute. We were running only on small electrodes. I cannot calculate revolutions per minute into feet per second off-hand.

MR. SPERRY: What size electrode?

PROF. BANCROFT: Electrodes of about a centimeter in diameter.

MR. SPERRY: And velocity of 200?

PROF. BANCROFT: Anywhere from 200 to 1,200 revolutions per minute.

MR. L. D. VORCE: I would like to ask about the element of time. There is nothing said in the paper about how long the electrolysis was continued before these determinations were made.

PROF. BANCROFT: These were only run for a short time, because the object was merely to see what the preliminary conditions for deposition were. Of course, in some of these cases the deposit was necessarily somewhat larger, and the longer you run it the worse the deposit will get. That is true of any current density whatsoever, and how soon things would begin to go bad I do not know, but it is simply a question of the general roughening of the deposit. We hope, within the next three or four years, to have a larger power equipment than now, and when we do get it we will try to have some of these things on a scale larger than electrodes the size of a lead pencil.

A paper read at the Eleventh General Meeting of the American Electro-chemical Society, at Philadelphia, Pa., May 3, 1907, President Carl Hering in the chair.

THE ELECTROLYTIC DEPOSITION OF NICKEL-ZINC ALLOYS.—II.*

BY EUGENE P. SCHOCH AND ALCAN HIRSCH.

When a solution which contains both nickel and zinc salts is electrolyzed, the metal deposit obtained is always an alloy of both metals. Furthermore, the proportion of zinc in the deposit is surprisingly large, particularly in view of the difference between the single potentials of nickel and zinc respectively, as given by Neumann.[1] Though Muthmann and Fraunberger[2] found that the difference between the single potentials of the two metals is less (only about 0.17 volt), yet even in view of this the per cent. of zinc in the alloys is remarkably large. We have presented, in a recent publication,[3] some details concerning the deposition and composition of the alloys obtained with different current densities from four different solution mixtures of the sulphates of these metals. The results there presented show that the ratio of zinc to nickel (by equivalents) in an alloy is from 4.5 to 14 times their ratio in the electrolyte, depending upon the total concentrations in the latter of the salts of the two metals. These solutions exhibit a noticeable tendency to produce with all larger current densities an alloy of particular composition. When the solutions employed are of moderate concentrations, and the sum of the equivalents of the two metals is the same in all solutions, then the "constant" alloys obtained with large current densities contain the zinc and nickel in a ratio (by equivalents) equal to 5.3 times their ratio in the electrolyte. This is as far as the first paper extends.

In continuing the work, the first object was to prepare alloys higher in nickel. The following alloys were prepared by the same method as that employed in the first paper, except that

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* Contribution I appeared in the Journal Am. Chemical Society, 1907, p. 314.

[1] Z. Phys. Chem., *14*, 229.

[2] Math.-phys. Kl. d. K. Bayr. Ak. D. W., *34*, Vol. 2 (1904).

[3] J. Am. Chem. Soc., *39*, 314.

small lead pipes were used as cathodes, and hence a much smaller amount of deposit was needed.

TABLE I.

No.	C.D.	Per cent. of Theoretical Yield.	Wt. of Alloy.	Per cent. Ni in Alloy.	Ni : Zn in Electrolyte. (by equivalents)
1	0.6	42	0.3496 gm.	20	4 : 1
2	0 5	30	1.0895 gm.	32.2	4 : 1
3	0.1	26	0.0326 gm.	19	6 : 1
4	0.4	31	0.4970 gm.	25	6 : 1
5	0.4	23	0.0370 gm.	42.4	26 : 1

Composition of the electrolytes used in making the alloys presented in Table I (in each case the total volume is 2 liters):

No. 1—350 cc. 2 N. nickel sulphate; 75 cc. 2.5 N. zinc sulphate; 30 gm. aluminium sulphate.

No. 2—Same as in No. 1.

No. 3—350 cc. 2 N. nickel sulphate; 50 cc. 2.5 N. zinc sulphate; 30 gm. aluminium sulphate.

No. 4—Same as in No. 3.

No. 5—330 cc. 2 N. nickel sulphate; 10 cc. 2.5 N. zinc sulphate; 30 gm. aluminium sulphate.

It is seen that the yield is very low. Many attempts resulted in powdery deposits which were not analyzed. With a solution of this kind, good deposits still higher in nickel could not be obtained. It appears to be particularly difficult to get a good plate from these solutions when they contain only a few per cent. of zinc. This presents itself strikingly as follows: A good plate of nickel is first deposited from a pure nickel sulphate solution. Then as much zinc sulphate as amounts to two or three per cent. of the nickel sulphate is added. A powdery deposit is formed immediately with any current density.

This peculiarity in the behavior of the sulphate solutions is due to a great difference in overvoltage or excess tension of the different alloys. The alloys with 20 per cent. and less nickel present essentially a "zinc" surface—they are solutions of nickel in zinc. This opinion is based (1) on the experiments which were made to prepare these alloys by fusion, and (2) on the potentials of the alloys against zinc in zinc sulphate solution, which are listed further on in this paper. The evolution of hydrogen from such surfaces, at the potentials at which the depositions take place, is slight. All alloys with a *greater* per cent. of nickel, however, exert a much smaller excess tension, and hence the evolution of hydrogen takes place to a large extent. The extensive evolution of hydrogen interferes with the formation of a reguline deposit, and also possibly affects the ratio in which the two metals are deposited.

Ammoniacal solutions were tried next to produce alloys high in nickel. The details are presented in Table II.

TABLE II.

No.	C.D.	Temp.	Per cent. of Theoretic'l Yield.	Wt. Alloy.	Per cent. Ni.	Composition of Electrolyte.
6	1.4	25	42	0.2326 gm.	23.9	Nickel amm. sulph., 15 gm. Zinc sulphate, 10.8 gm. Amm., Sp. Gr., 0.90, 60 cc. Total volume, 950 cc. Ratio Ni : Zn, 1 : 1
7	1.0	25	31	0.4047 gm.	39	Nickel amm. sulph., 60 gm. Zinc sulphate, 9 gm. Amm., Sp. Gr., 0.90, 5 cc. Total volume, 1 L. Ratio Ni : Zn, 5 : 1.
8	0.5	25	15	0.0612 gm.	36.8	Same as in No. 6.
9	1.0	25	15	0.1848 gm.	59	Nickel amm. sulph., 60 gm. Zinc sulphate, 2.9 gm. Amm., Sp. Gr., 0.90, 60 cc. Total volume, 1 L. Ratio Ni : Zn, 15 : 1.
10	0.5	25	17	0.0717 gm.	63	Nickel amm. sulph., 15 gm. Zinc sulphate, 1.1 gm. Amm., Sp. Gr., 0.90, 30 cc. Total volume, 900 cc. Ratio Ni : Zn, 10 : 1.
11	—	25	—	0.0208 gm.	68.2	Nickel sulphate, 10 gm. Zinc sulphate, 2.7 gm. Amm., Sp. Gr., 0.90, 100 cc. Total volume, 900 cc. Ratio Ni : Zn, 4 : 1.
12	1.4	25	39	0.2134 gm.	76.5	Same as in No. 10, Ratio Ni : Zn, 10 : 1.
13	0.5	25	33	0.0660 gm.	76.8	" " " "
14	0.5	25	23	0.0670 gm.	64.4	" " " "
15	0.5	50	19	0.0374 gm.	88.9	" " " "
16	0.5	50	23	0.0412 gm.	64.7	" " " "

NOTE:—In these experiments the deposit was made upon small platinum tubes, because the per cent. of zinc was low enough not to affect platinum. Otherwise the experimental arrangement was essentially the same as before.

Here, again, the yield is very low. The deposits, however, are reguline, though they present a dull, dark surface.

The marked tendency to deposit a relatively large proportion of zinc is also shown by these ammoniacal solutions. Hence our attention was next directed to gather facts that would elucidate the cause of the large per cent. of zinc. Towards this end the following experiments were made:

(1) Deposition of alloys high in nickel on a mercury cathode;

(2) Determination of the cathodic polarization or deposition potential on a mercury cathode during the electrolysis of solutions of nickel sulphate, zinc sulphate, and mixtures of these, with various current densities.

(3) Measurements of the potentials of the alloys against zinc in normal zinc sulphate solution.

(4) Preparation of some nickel-zinc alloys by fusion.

(5) Determination of the equilibrium conditions of nickel, zinc, and their alloys, with solution mixtures of their sulphates.

1. Deposition of alloys high in nickel on a mercury cathode.

As mentioned above, the extensive evolution of hydrogen probably affects the ratio in which the metals are deposited. Since the excess tension of mercury and amalgams is very high, it was easily foreseen that these alloys could be deposited in a mercury cathode without the evolution of hydrogen.

The experimental arrangement used was the following: A small beaker, which contained just enough pure mercury to completely cover the bottom, was weighed, together with a stout platinum wire. The beaker and contents were placed in a glass jar. The electrolyte flowed from an elevated bottle into the beaker through two glass tubes at a rate of about one-half liter per minute. The total quantity of electrolyte employed was large (12 liters) so that the liquid layer in contact with the cathode was of constant composition during an experiment. Of course, the overflow was periodically pumped back to the elevated bottle. The platinum wire which dipped into the mercury cathode was protected by a small glass tube which just reached the mercury surface. A platinum spiral served as anode. The deposited alloy, together with the platinum wire and beaker was washed, dried with alcohol and ether, and weighed. The alloy and mercury were transferred to a small casserole and heated with dilute nitric acid. After all the alloy was dissolved, the liquid was decanted into an evaporating dish, and the undissolved mercury well washed. Dilute sulphuric acid was added to the solution, and the mixture evaporated to dryness. The residue, which contained a great deal of insoluble basic sulphate of mercury, was leached out repeatedly with hot water acidulated with sulphuric acid. The hot solution was treated with hydrogen sulphide, filtered, and the solution washed until free from nickel salts. The filtrate was analyzed for nickel in the usual way, and the zinc determined by difference. The results obtained with a mercury cathode are presented in Table III.

TABLE III.

No.	Ratio Zn : Ni in Solution. (by equival'ts)	Wt. Alloy.	Per cent. Ni.	Composition of Electrolyte.
17	2 . 98	1.6480 gm.	69.5	12 L. N/1 nickel sulphate; 240 cc. N/1 zinc sulphate.
18	4 : 96	1.0440 gm.	69.2	Total volume, 12 L., 4 % of which was zinc sulphate (N/1) and 96% nickel sulphate (N/1).
19	7 : 93	1.2920 gm.	62.5	Total volume, 12 L., 7% of which was zinc sulphate (N/1) and 93% nickel sulphate (N/1).
20	11 : 89	2.3580 gm.	44.2	Total volume, 12 L., 11% of which was zinc sulphate (N/1) and 89% nickel sulphate (N/1).
21	20 : 80	2.1722 gm.	34.2	Total volume, 12 L., 20% of which was N/1 zinc sulphate, and 80% N/1 nickel sulphate.
22	½ : 99½	1.8780 gm.	100	Total volume was 8 L., ½% of which was N/1 zinc sulphate and 99½% nickel sulphate (N/1).

NOTE.—In these experiments the current density was high (C.D.=2.5 amp. per sq. dcm). The current efficiency was very nearly 100 per cent. in all experiments.

While it cannot be denied that the mercury cathode might influence the ratio of nickel to zinc in the deposit, yet any such influence is likely to be small, because the cathodic polarization remains steadily constant in any one operation, even after a very stiff amalgam has separated at the top. This was specially ascertained by trial. Assuming, then, that the influence of the mercury cathode is slight at most, we may compare the results with those previously obtained with lead cathodes.

To do this, the factors with which the ratios of zinc to nickel (by equivalents) in the electrolyte must be multiplied to give the ratios of zinc to nickel (by equivalents) in the alloy, have been calculated. However, only those experiments are considered here in which the current efficiency is 100 per cent., or nearly so, and the current density at least 1.5 amperes. The results appear in Table IV.

TABLE IV.

Reference No.	Ratio Zn : Ni in Alloy. (by equivalents)	Ratio Zn : Ni In Electrolyte. (by equivalents)	Factor.
This paper 17	0.49 : 1	0.02 : 1	21.1
" " 18	0.50 : 1	4 : 96	12
" " 19	0.66 : 1	7 : 93	8 9
" " 20	1.4 : 1	11 : 89	11
" " 21	2.1 : 1	1 : 4	8 4
First paper 9 (loc. cit.)	7 : 1	0.6 : 1	11.7
" " 13	13 : 1	2.98 : 1	4.3
" " 15	4 : 1	0.3 : 1	13.3
" " 19	24 : 1	3.3 : 1	7.3

It is seen that the factor is largest in Exp. 17 of this paper. That is, the main cause of the large per cent. of zinc in the alloys has its maximum effect under the conditions in this experiment. With either less or more zinc in the electrolyte the cause is less effective. Exp. 22 of this paper should be specially noted in this connection. The significance of these facts will be discussed farther on.

2.—*Determination of the cathodic polarization on a mercury cathode.*

Measurements of the cathodic polarization had been attempted during the deposition of nearly all the foregoing alloys, but the results are of no value, on account of their extreme irregularity. This is due to the evolution of hydrogen, the same cause which has heretofore prevented the determination of the discharge potential of nickel and zinc. Though Le Blanc[3] reports having obtained the discharge potential of zinc, he did not get the

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[3] Z. Phys. Chem., *12*, 333.

characteristic sharp turn in the curve indicative of the decomposition point, but merely obtained the potential of the deposited zinc. With nickel the phenomenon of passivity prevented his getting even that much of a result. Since it was extremely desirable to get the discharge potential of the metals and their alloys, many trials were made to get a suitable experimental arrangement. In this connection a number of metals which exert high excess tension were tried as cathodes, but only mercury was found to be serviceable. With cathodes of this metal, results could be duplicated closely, and they also harmonized well with each other. The only serious objection that might be raised against the use of this cathode is the fact that the formation of amalgams would lower the discharge potential.[4] However, with sufficiently high current densities this effect is eliminated, as is shown by the fact that the value for zinc obtained by this method (1.050 volts against a normal calomel electrode) checks fairly well with the accepted value for its potential (1.053 volts[5] against a normal electrode).

The experimental arrangement employed in these measurements was the following: A large accumulator was short-circuited through a German silver wire of such length and thickness that about 0.5 ampere flowed steadily through the wire without heating it excessively. By means of a suitable mechanical arrangement, any fraction of the total voltage could be "tapped off" and applied to the poles of the electrolytic cell. By means of a pole-changer, the direction of the current could be reversed. A standardized Weston voltmeter (5 volts range) was connected in the circuit so as to show the voltage "tapped off." A Weston milli-ampere meter (range 150 milli-amperes) was inserted in the circuit, which passed through the electrolytic vessel.

The electrolyzing vessel employed for very small currents ("zero" up to C.D. = 0.005 amp.) was arranged as follows: A glass tube with a flat bottom (diam., 2.2 cm.; height, 10 cm.) was placed in a medium-sized beaker. The bottom of the tube was covered with mercury, and the beaker filled above the top of the tube with the liquid to be examined. A platinum wire, covered with a glass tube, made electrical connection with the

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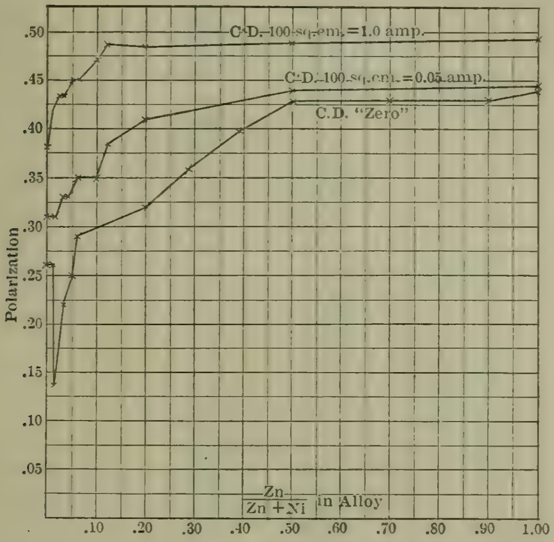
[4] Coehn and Dannenberg, Z. Phys. Chem., *38*, 609.

[5] Le Blanc, Text-book of Electrochemistry, tr by Whitney and Brown, page 248 (1907.)

mercury. A small porous cup was filled with N/1 $ZnSO_4$ solution and closed with a rubber stopper carrying an amalgamated zinc rod. This arrangement was used as a working pole of definite E. M. F., so that the voltage shown by the voltmeter, plus or minus the potential of this pole, gave the E. M. F. impressed upon the mercury pole. The C. R. drop through the solution was very small, because the current was small, and contact through the porous cup was quite extensive. The liquid over the mercury pole was not contaminated, because the cup was porous only on the bottom, and the bottom was at a lower level than the top of the tube containing the mercury. The capillary connecting tube of a normal calomel electrode also dipped into the liquid in the beaker. The calomel electrode and the mercury cathode were connected in a circuit containing a potentiometer and a capillary electrometer. This latter circuit and the primary electrolyzing circuit were both connected through a multiple point switch in such a manner that the primary current circuit was closed and the circuit through the calomel pole open. On depressing the handle of the switch, the primary was first broken, and then the calomel pole circuit closed. The switch had to be depressed and released very quickly. With a little practice in operating the switch, maximum polarization values could be accurately measured. All measurements were duplicated several times.

With larger electrolyzing currents, the surface layer of liquid over the mercury naturally would be impoverished, and thus the result would be affected. Hence it was necessary to keep the liquid flowing over the mercury. Also, since with larger currents the voltage impressed upon the electrolytic cell is used up appreciably in the C. R. drop, it was useless to measure it, and hence a platinum wire was used as an anode in place of the zinc pole previously employed. The vessel used was a small bottle with a cross-section of 8.04 sq. cm. The neck was closed with a rubber stopper through which passed an inlet and an outlet tube for the liquid, electrical connection for the cathode, and the platinum wire to the anode. The calomel electrode dipped into the funnel-shaped inlet tube. The liquid to be examined was kept flowing through the vessel during the time that the observations were made. The rest of the arrangement was essentially the same as before.

The results are given in Table V, A and B. Table V, A gives the results with small currents, and Table V, B gives the results with larger currents. The results with "zero" current and with two larger current values have been plotted by taking $\frac{\text{Ni}}{\text{Ni} + \text{Zn}}$ as abscissas, and the polarization values as the ordinates.



The polarization values given in the tables are the values observed against the normal calomel electrode, with the value of the latter assumed to be —0.56 volt.

In Table V, A, the column marked "E. M. F. impressed" gives the reading of the voltmeter, plus or minus the value of the zinc pole, assumed at 0.493 volt.

TABLE V—A.

*Ratio Ni : Zn in Solutions.	Milli-amps per 32 sq. cm.	E.M.F. impressed	Polarization.	Solution.	Milli-amps	E.M.F.	Polarization.
199 : 1	⅛—	.29	0.26	N/1 $ZnSO_4$	0	.40	0.41
"	⅛	.37	0.27	"	0	.49	0.41
49 : 1	0	.13	0.12	"	$\frac{1}{10}$—	.52	0.43
"	⅛	.17	0.14	"	¼	.55	0.45
32 : 1	0	.17	0.14	"	½+	.59	0.47
"	⅛	.29	0.22	N/1 $NiSO_4$	0	.24	0.18
24 : 1	0	.29	0.24	"	0	.29	0.22
"	⅛	.32	0.25	"	0	.31	0.23
19 : 1	0	.30	0.26	"	0	.33	0.24
"	$\frac{1}{10}$	.34	0.29	"	$\frac{1}{10}$	.38	0.26
"	⅛	.37	0.30	"	¼	.39	0.30
"	¼	.48	0.36	"	¼	.41	0 31
9 : 1	0	.29	0.24	"	½	.43	0.32
"	⅛	.34	0.30	"	½	.45	0.32
8 : 2	0	.31	0.28				
"	0	.34	0.25				
"	⅛	.35	0.32				
"	⅛+	.41	0.34				
"	¼	.43	0.38				
7 : 2	0	.34	0.26				
"	⅛	.45	0.36				
"	⅛+	.47	0.41				
"	¼	.49	0.49				
5 : 2	0	.37	0.34				
"	$\frac{1}{10}$	.45	0.39				
"	¼	.48	0.40				
5 : 5	0	.46	0.42				
"	$\frac{1}{10}$	.49	0.43				
3 : 7	0	.38	0.36				
"	⅛	.45	0.41				
1 10	⅛	.45	0.43				

* The total sum of normalities in all cases was N/1.

The first result to be considered is the discharge potential of nickel. The close agreement in the case of the discharge potential of zinc, which was pointed out above, allows us to expect the same for the discharge potential of nickel. The discharge potential of nickel as found (0.38 volt) agrees with the value of the potential of nickel found by Muthmann and Fraunhofer (0.32 volt) in so far as it places the value much higher than where earlier investigators placed it. Our value is still about 0.06 volt higher than that found by Muthmann and Fraunhofer, as is shown by the numerical values given above. We are inclined to believe that our result is more nearly correct, because the equilibrium experiments given farther on indicate that the

TABLE V—B.

*Ratio Ni : Zn in Solutions.	Milli-amps. per 8.04 sq. cm.	Polarization.	Solution.	Milli-amps	Polarization.
99 : 1	2	0.31	88 : $NiSO_4$ 12 : $ZnSO_4$	2	0.44
"	4	0.36			
"	7	0.39	"	4	0.45
"	10	0.39	"	7	0.46
"	40	0.41	"	10	0.47
"	80	0.41	"	40	0.48
"	120	0.41	"	80	0.49
"	150	0.41	"	150	0.49
49 : 1	2	0.33	N/1 $NiSO_4$	2	0.32
"	4	0.37	"	4	0.33
"	7	0.40	"	10	0.35
"	10	0.41	"	80	0.38
"	40	0.43	"	120	0.37
"	80	0.44	"	150	0.38
"	120	0.44	N/1 $ZnSO_4$	2	0.41
"	150	0.44	"	4	0.42
32 : 1	2	0.33	"	7	0.44
"	4	0.37	"	10	0.44
"	7	0.41	"	40	0.47
"	10	0.43	"	80	0.48
"	40	0.43	"	200	0.49
"	80	0.43			
"	120	0.43			
"	150	0.43			
19 : 1	2	0.35			
"	10	0.45			
"	40	0.45			
"	120	0.44			
"	150	0.44			
16 : 1	2	0.35			
"	4	0.39			
"	7	0.43			
"	10	0.43			
"	40	0.45			
"	80	0.45			
"	120	0.45			
"	150	0.46			
9 : 1	2	0.35			
"	4	0.39			
"	7	0.41			
"	10	0.43			
"	40	0.46			
"	80	0.47			
"	120	0.47			
5.7 : 1	2	0.38			
"	10	0.43			
"	40	0.46			
"	80	0.49			
"	150	0.49			
4 : 1	2	0.41			
"	40	0.46			
"	120	0.48			
1 : 1	2	0.41			
"	10	0.43			
"	40	0.46			
"	150	0.48			

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* Sum of normalities in all cases, N/1.

potentials of nickel and zinc are very close together—even closer than 1-10 volt. And, finally, it would not be surprising if Muthmann and Fraunhofer's method of preparing the nickel surface, though very successful, had not been able to overcome entirely the natural tendency to assume a lower potential. We shall submit this method to further trial, and shall also determine the values for metals, such as iron and cobalt, which present the same difficulties.

The measurements made with the solution mixtures of zinc sulphate and nickel sulphate will be considered next. From a study of the results it was found that the measurements made with small or "zero" currents are very significant, while the others are less so. Of course, these "zero" current measurements may all be affected by the influence due to the formation of amalgams—the potentials may all be lower than they should be. But they are approximately correct relative to each other. Thus considered, they show that starting with nickel sulphate the discharge potential of alloys becomes rapidly less, reaches a minimum with 2 per cent. zinc sulphate (by equivalents) in solution, then rises steadily and reaches the maximum value, equal to the discharge potential of zinc when the solution contains 30 per cent. zinc sulphate (by equivalents). By referring to the results with higher current densities, it is seen that a solution with only 10 per cent. zinc sulphate exhibits the maximum discharge potential.

The most significant part of the results, however, is the minimum point shown with "zero" current in a solution containing 2 per cent. zinc sulphate. This point is approximately 0.35 volt below the discharge potential of zinc from N/1 $ZnSO_4$, and 0.25 volt below that of nickel from N/1 $NiSO_4$. The absolute discharge potential of this alloy deposited from a solution mixture of nickel and zinc sulphates containing 2 per cent. of the latter may be somewhat higher. This minimum point shows itself so clearly, even through the E. M. F. impressed, that there can be no mistake about its existence. Now, it may be recalled that a solution mixture containing 2 per cent. zinc sulphate deposited nickel and zinc in the mercury cathode in the ratio 69.5 per cent. nickel, 30.5 per cent. zinc, and that in this case the effect which produced the remarkably large proportion of zinc in the alloy is at its maximum. Furthermore, by referring to the table of the potentials of the alloys against zinc in N/1 $ZnSO_4$ solution, given farther on (Table VI), it will be seen that an alloy of this composition would show a difference of potential against zinc equal to 0.42 volt, which agrees approximately with the value of the minimum discharge potential given above. It appears that this minimum discharge potential is a very significant point, and that it has been approximately correctly located, and its properties recognized.

3. Potentials of the alloys against zinc in N/1 $ZnSO_4$ solution.

Following the work of other investigators,[6] the potentials of the alloys against zinc in N/1 $ZnSO_4$ solution were measured. The measurements were made with the aid of a potentiometer and a capillary electrometer. The results are given in Table VI. All alloys with less than 20 per cent. nickel have a very small or "zero" potential against zinc, which fact supports the view that they are solutions of nickel in zinc. When the amount of nickel in the alloy reaches about 24 per cent., the potential difference suddenly increases by about 0.25 volt. With the alloys immediately following the results are irregular. Both the sudden change in the potential and the irregularity of the results are probably due to the following cause: About 24 per cent. nickel is the limit of the solubility of nickel in zinc (as shown under *4*, below), and with a greater per cent. of nickel other "phases" are formed which have a much lower excess tension. These permit the evolution of much hydrogen, which probably affects the ratio in which the two metals are deposited. Whatever may be the cause, it is certain that with a solution from which an alloy of approximately 25 per cent. nickel may be obtained, the deposit may change suddenly from a bright and "zincy" surface, on which very little hydrogen is evolved, to a dull, dark surface, on which a great deal of hydrogen is liberated. If the alloy at the end of the operation has a bright surface, its potential against zinc is slight, whereas if it has a dull surface, its potential against zinc is much greater.

The alloys with more than 27 per cent. nickel show regularly a greater potential against zinc. It must be realized, in this connection, that it is the zinc in the alloy that determines the potential against zinc. With two metals such as nickel and zinc,

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[6] **Herschkowitsch, Zeit. Phys. Chem., *27*, 123; Shepherd, J. Phys. Chem., *7*, 15; and others.**

whose potentials are close together, it might be a question as to which one exerts the greater potential in an alloy. But the phenomenon of passivity prevents the nickel from exhibiting any potential, and hence under these conditions the potential observed is always that of zinc.

TABLE VI.

Per cent. Nickel in Alloy.	Potential of Alloy Against Zinc in N/1 Zinc Sulphate Solution.
5.8	0.0+
8.4	0.0+
10.8	0.013
19.1	0.084
21	0.084
24	0.329
25	0.084
27	0.329
36.8	0.370
63+	0.412
64.4	0.412
64.7	0.412
76.5	0.432
77	0.484
88.9	0.535

On the other hand, nickel also must have a certain potential in each alloy, even though the phenomenon of passivity prevents its measurement. This potential cannot be greater than the discharge potential of the alloy, and since the discharge potentials of nickel sulphate solutions decrease with admixture of zinc sulphate to a minimum point corresponding to the addition of 2 per cent. zinc sulphate, it follows that the potential of nickel also becomes less with increasing per cent. of zinc in the alloy.

The curve of decreasing potentials of zinc in these alloys and the corresponding curve for nickel must cross each other; at this point the potentials must be equal, and hence equal to the discharge potential. This point of intersection must coincide with the "minimum" point mentioned before.

Thus we have arrived at the following conclusion of the question under consideration: The alloying of nickel with zinc reduces the potential of both, the mutual specific effect being such that in an alloy of approximately 70 per cent. nickel, 30 per cent. zinc, the potentials of the two constituents are equal to each other and equal to the discharge potential from a solution containing 2 per cent. zinc sulphate, 98 per cent. nickel sulphate (by equivalents). Under these conditions, the proportion of zinc obtained in the alloys is at its maximum, and the discharge potential of the solution mixture is at the minimum.

4.—Preparation of alloys by fusion.

A Buffet assay crucible was lined with a stiff mixture of finely-powdered charcoal and molasses, and then heated to bake the lining.[7] Lump zinc and shot nickel were weighed in the desired proportions, with an allowance for volatilizing some of the zinc. The mixture was placed in the crucible and covered with a layer of powdered borax and charcoal. The mass was heated somewhat above the melting point of zinc, but not to the point of volatilizing the zinc extensively. The alloying of the metals is attended with the evolution of a great deal of heat, so that frequently the temperature became excessive, and the crucible had to be taken out of the furnace to allow it to cool slightly. The molten mass was stirred with an electric light carbon, and finally allowed to cool in the crucible.

It was found that the maximum allowable temperature of fusion prevented the preparation of any alloys with more than 25 per cent. nickel; a mixture with more than 25 per cent. nickel resulted in a fused mass which contained some of the original shot nickel scattered through the mass. Even the 25 per cent. nickel alloy showed traces of unalloyed nickel. The homogeneous alloys obtained were finely powdered, carefully sampled, and analyzed. A number of these alloys were used for experiments given under 5.

From the results we may gather that nickel dissolves in molten zinc up to 25 per cent. (nearly), and that alloys with a greater per cent. of nickel have a melting point far above the boiling point of zinc, and hence cannot be prepared by this simple method.

5.—Determination of equilibrium conditions of zinc, nickel, and their alloys, with solution mixtures of their sulphates.

Only a few final results can be presented under this heading, though the experiments undertaken have been many more in

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[7] Kindly suggested by Dr. Harper, of this laboratory.

number, and the object in view much broader. The mixtures, together with pieces of cracked glass, were put in well-stoppered bottles, which were tied to the side of a slowly revolving wheel. Thus the solids were ground and the liquid shaken thoroughly. All trials were made at 25°. The following experiments may be presented as final results:

(a) Zinc dust was shaken with a solution of nickel sulphate so as to precipitate a small amount of nickel upon the zinc. The mixture was filtered and washed, first with water and then with some of the solution with which it was to react afterwards. Portions of this zinc dust were treated separately with solution mixtures containing nickel and zinc sulphates in various proportions, some less, and others much more than 2.2 per cent. nickel sulphate (by equivalents), and in each case equilibrium was attained when the solution contained 2.2 per cent. nickel by equivalents. The total concentrations of the solutions ranged from double normal to half-normal. At least 20 grams of zinc dust were used with 50 cc. of solution. The mixtures attained equilibrium in a few hours.

(b) Excess of nickel powder, reduced by hydrogen, was shaken with N/2 zinc sulphate solution for forty hours; the resulting solution contained 14+ per cent. nickel sulphate (by equivalents). The powder was filtered and washed, and then treated with another portion of N/2 zinc sulphate solution for sixty hours; the resulting solution contained 10 per cent. nickel sulphate (by equivalents). Another fresh portion of nickel powder shaken with N/10 zinc sulphate solution for forty hours produced a solution containing 12 per cent. nickel (by equivalents).

In connection with these results we must recall the fact that nickel lowers the discharge potential of zinc, and zinc lowers the discharge potential of nickel. Hence zinc should discharge "into" a cathode of nickel at a much lower discharge potential than its own proper potential, and since the potentials of nickel and zinc differ by 0.1 volt only, it is to be expected that an excess of finely powdered nickel acting on zinc sulphate solution would displace the zinc extensively. This is borne out by the facts given under *(b)*, above. Also, nickel should deposit "into" a cathode in which it alloys with zinc at a discharge potential very much lower than its own potential. Hence, excess of zinc in contact with a solution of nickel sulphate should precipitate the nickel even more extensively than the extent calculated from the difference of their single potentials (0.493 — 0.380 = 0.113 volt). The final proportion of nickel and zinc respectively in the solution should be much less than that calculable by Nernst's formula—about 1 : 10,000. However, the proportion determined experimentally is 1 :50, approximately. This disagreement is certainly surprising.

Finally, it may be pointed out here that the mutual precipitation of nickel and zinc as under *(a)* and *(b)*, above, should *not* produce the same solution mixtures, because the solid phases at the bottom of the mixtures are essentially different. In this respect the results under *(a)* and *(b)* harmonize.

Work on this problem will be continued.

Chemical Laboratory, University of Texas,
April 15, 1907.

DISCUSSION.

DR. W. D. BANCROFT: I think this is a very interesting paper that Dr. Schoch has presented, and I hope that he will continue the work. There are two or three things that occur to me. In the first place, I think one of the difficulties in measuring the decomposition voltage of nickel is due to the fact that there is no such thing as a reversible nickel electrode. We have tried a great many experiments with nickel quite recently, and in no case is the nickel electrode strictly reversible.

The second point is, that it does not seem to me quite suitable to reason from the precipitation of nickel and zinc by themselves, to the precipitation of nickel and zinc in mercury. I am inclined to think that there will necessarily be very wide differences under those circumstances as regards the ratios and everything else.

The third point I should like to make is that it would be very desirable if Dr. Schoch would take his nickel-zinc alloys and put them under the microscope, to find out what he has got. I think it is perfectly safe to say that his results cannot possibly be explained on the assumption that he has nickel and zinc side by side in a two-phase system; he must have either a solid solution or compounds, and we cannot discuss the subject rationally until we know exactly what precipitates from these solutions.

Mr. Schoch: I wish to state that I was not able, in these few minutes, to touch upon more than a small part of the work. Work of this sort, to be of any value, must be comprehensive. Thus we have also made the alloys by fusion; we have started to determine the heats of solution of the alloys, and we are preparing to examine them microscopically. Of course, we can report only a portion of the work at present. One of the most interesting portions, which will appear in print, but which could not be given here, under the circumstances, is the results of the determinations of the deposition potentials of the alloys.

A paper read at the Eleventh General Meeting of the American Electrochemical Society, in Philadelphia, Pa., May 3, 1907, President Carl Hering in the chair.

THE EFFECT OF STRESS UPON THE ELECTROMOTIVE FORCE OF SOFT IRON.

By William H. Walker and Colby Dill.

When viewed in the light of the modern theory of solutions, and Nernst's conception of the source of the electromotive force between a metal and a solution, the corrosion of iron in water is seen to depend essentially upon three factors. These are the electrolytic solution pressure of the iron, the elctrolytic solution pressure of the hydrogen, and the condition of the surface of the iron, or metal which is in contact with the iron, in so far as it affects the ease with which molecular hydrogen may be liberated upon it (so-called excess voltage). For any given experiment the two latter may be held practically constant, and the electromotive force of the system made to depend for the greater part upon this solution pressure or escaping tendency of the iron. Any condition which affects this tendency to dissolve (if we grant the assumption that a definite relation exists between electromotive force and corrosion) is therefore of importance in a consideration of the general subject of the causes of corrosion of iron and steel.

One of the conditions which is supposed to influence the electromotive force of iron, and which has received considerable attention of late, is the effect of stress upon the metal. The literature upon this subject is quite as contradictory as it is voluminous. In that most recent work dealing with the corrosion of iron, Wood's "Rustless Coatings; Corrosion and Electrolysis of Iron and Steel,"[1] under the heading "Corrosion Increased by Stress" (page 348), the most weight is laid on the work of two investigators, the results of whom are given in full; but one communication of importance has appeared on the subject since this work was published.

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[1] Wiley & Sons, New York, 1904.

The first authority quoted as worthy of a hearing is Thomas Andrews.[2] When considered from an electrochemical standpoint, his work is found to be rather unsatisfactory. His method of experimentation may be best shown by giving a typical experiment at some length:

"From a bar of each of the metals under investigation, a portion was cut and turned to the dimensions given by Fig. 1. This piece was then placed in a suitable tensile testing apparatus and submitted to a stress, in most cases sufficient to produce an elongation of 20 per cent. between gage points 3 inches apart. After having been strained, the piece was cut in two at the center. . . . . The strained end A was left untouched in the lathe up to the point where there was any reduction in the diameter caused by the tensile stress, just as it came from the testing machine, and the unstrained end, B, of the other half was turned exactly to the dimensions of the piece A.

"The two halves A and B were then immersed as a galvanic couple in a saturated solution of sodium chloride, and in some of the experiments on torsional stress, in sea water as an electrolyte. . . .Galvanic contact between the two pieces of metal was made only momentarily at the time of reading the galvanometer, and the difference of potential between the 'strained' and the 'unstrained' metals thus observed. . . .

"A sensible current was observed between the two bars, and the 'unstrained' portion of the metals experimented upon was found to be in the electropositive position, answering to the zinc in a galvanic couple. This indicated that the 'unstrained' metal was being more rapidly acted upon by the solution, and was thus being corroded more rapidly than the 'strained' metal."[3]

The average electromotive force obtained between strained and unstrained portions of the same metal were:[4]

Wrought-iron forged shafts....................	.016 volt.
Soft Bessemer steel forged....................	.019 "
Hard " " "	.006 "

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[2] Proc. Inst. Civil Eng. (British), *118*, 356 (1894).

[3] A most lamentable error occurs in Wood's presentation of Andrews' work. In summing up the conclusions drawn, he says that the *strained* portions were found electropositive, while Andrews states just the opposite.

[4] *Loc. cit.*, p. 253.

Soft cast steel	.003	volt.
Hard “ “	.003	“
Silicon steel	.004	“
Aluminum steel	.004	“
Nickel steel	.003	“
Rolled wrought-iron bars	.002	“
Soft Siemens steel	.005	“
Hard “ “	.005	“
Copper steel	.006	“
Chromium steel	.001	“
Bessemer-steel hammered forgings	.011	“
Siemens “ “ “	.006	“

These results may be said to point to the conclusions reached by Andrews; but his use of a solution of common salt as an electrolyte for potential measurements is most unfortunate, owing to the magnitude of the polarization phenomena which are always observed when a sensible current is allowed to flow through such a cell. In any case, this work furnishes no information concerning the effect of stresses below the elastic limit, such as are more generally met with in engineering practice, for the specimens were strained until an elongation of 20 per cent. in 3 inches had been produced, and such a strain is far beyond the elastic limit.

The second authority mentioned by Wood, and one whose work is quite generally quoted by engineers, is Hambuechen.[5] His investigation determined, among other things, the change in electromotive force of wrought iron, Bessemer steel, machinery steel, tool steel, copper, brass, zinc, and other metals, from zero stress to breaking. The load was applied in a testing machine, and the potentials were measured by the well-known Poggendorff compensation method. A capillary electrometer of great sensitiveness was used as an indicating instrument, and the electrolyte was ferric chloride. His results are presented in the form of curves giving the change of electromotive force with stress, and they seem to show striking relations. In every case, the electromotive force rises with increasing stress, thus indicating increased tendency to corrode.

In six tests upon wrought iron, the rise in electromotive force

[5] Bulletin, Univ. Wisconsin, Eng. Series, *2*, No. 8, (1900).

from zero stress to about 20,000 pounds (which from the curves may be assumed to be the elastic limit) was as follows:

No. of Table.	Rise in Potential.	No. of Table.	Rise in Potential.
XIII	.0029 volt.	XVI	.0006 volt.
XIV	.0029 "	XVII	.0060 "
XV	.0006 "	XVIII	.0029 "

The results are irregular in several cases, showing that there were other variables which influenced the potential; the rise in electromotive force is nevertheless unquestionable.

There is reason, however, for believing that the rise in potential may not in any degree be due to the straining effect. When iron is immersed in ferric chloride solution, the potential is nearly zero at first, as Hambuechen says on page 246, but it rises rapidly, and does not reach equilibrium for many hours, owing to the action of the free acid always present in ferric chloride solutions, owing to hydrolysis. T. W. Richards and Behr[6] and Finkelstein[7] have found similar results.

The fact that Hambuechen gives the potential of iron against a ferric chloride solution as "very nearly zero," shows that he measured the potential before the latter had risen to its constant value. In view of this fact and of the fact that he makes no mention of allowing the potential to reach a constant value, one is driven to a consideration of the possibility that he made his measurements while the potential was rising. Any conclusions, therefore, that he has drawn concerning the effect of strain may be fallacious.

Hambuechen also repeated Andrews' experiment with soft iron, and was unable to duplicate the latter's results. He says: "Two iron test pieces of the dimensions given by him (Mr. Andrews) were prepared and placed in a testing machine, and subjected to a stress until an elongation of 23 per cent. in 3 inches was produced.

"Immediately upon immersing both pieces simultaneously into a solution of sodium chloride, the strained metal was found to be the negative pole of the cell; but after one or two minutes the cell reversed, the unstrained becoming the negative pole of

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[6] Electromotive Force of Iron and Occluded Hydrogen. Publications of Carnegie Institute of Washington, 1906.

[7] Zeitschr. physik. Chem., 39, 91.

the cell, and this condition appeared to be stable. It was found, however, that upon shaking the cell, or by taking out one piece of iron and then replacing it, almost any result could be obtained. . . .

"After allowing the test pieces to remain in solution for five hours, a measurement showed that the cell had again reversed, and that the strained metal was again the negative pole. Upon again standing over night, and then measuring the electromotive force, it was found that the strained metal was still the negative pole, although the amount of the electromotive force had decreased slightly." This is the opposite of the final results of Andrews.

In the investigation by Richards and Behr,[8] some experiments upon the effect of strain upon the potential of iron were made. The authors conclude from their work that the magnitude of the changes produced is smaller than is usually supposed. The data are, however, so scanty and the results, as the authors point out, so irregular that no conclusions of value can be drawn.

The present investigation was undertaken with the hope of throwing some light upon the question of the sign and magnitude of the potential changes caused by straining a piece of iron, particularly below the elastic limit.

The magnitude of the increase in potential which one would expect to be produced can be easily computed on the assumption that the energy stored up in the specimen below the elastic limit is all available as potential. Some very pure commercial iron (Swedish charcoal iron) was obtained and tested in the usual manner, to determine the modulus of elasticity and elastic limit. The diameter of the specimen was about 0.25 inch. Elongations were measured by means of a micrometer which could be read with fair accuracy to ten-thousandths of an inch. Electrical contact was used to insure parallel conditions at each reading. The results of this test showed the modulus of elasticity, or ratio of stress to strain, to be 28,000,000, and the elastic limit about 16,500 pounds per square inch. A second experiment gave concordant results. From this data, the amount of work which

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[8] *Loc. cit.*

would be done upon a cubic inch of iron, if it were strained to its elastic limit, would be

$$w = \int_0^{17000} fdl$$

where w = work done in inch pounds,
f = stress applied at each instant,
l = strain produced.

Since $\frac{f}{l} = 28{,}000{,}000$, $dl = \frac{1}{28000000}\, df$.

Substituting this value, $w = \frac{1}{28000000} \int fdf$

Integrating and substituting limits,

$$w = \frac{17000 \times 17000}{2 \times 28000000} = 5.16 \text{ inch-pounds.}$$

The maximum amount of work which it is possible to do upon one cubic inch of soft iron by stretching it to its elastic limit is therefore 5.16 inch-pounds. This is equal to 5.83 joules, and one cubic inch of soft iron weighs approximately 126 grams, assuming the specific gravity to be about 7.7. The work done in joules per equivalent is therefore

$$5.85 \times \frac{1}{126} \times \frac{56}{2} \text{ or } 1.30 \text{ joules;}$$

and the change in electromotive force which would be expected is $\frac{1.30}{96{,}600}$ or 0.0000134 volt. The magnitude of this change is thus very small; its direction should be positive, because it is the manifestation of energy stored up in the metal.

Apparatus.

The well-known method of Poggendorf was selected as the most suitable for the measurement of such small potential changes as seemed likely. The apparatus was arranged according to the diagram, Fig. 1.

The slide wires were clamped at the ends between plates of brass tightly screwed together, and the whole mounted upon a graduated wooden scale. The resistance boxes were of the ordinary plug type, and require no description. The coils have not as yet been calibrated, but since it is not primarily the object of this investigation to determine absolute potentials, but merely changes, an error in the value of the external resistance is not of serious consequence. In the potential measurements, different combinations of nominally equal resistances were tried, and were found to agree to 0.1 millivolt, and therefore the potentials given in the results are probably very nearly correct. The cadmium cell was made up with care according to the directions given by Ostwald,[9] and the value for its potential difference used in the following computation is 1.0185 volt.

The galvanometer was an unusually good instrument of the d'Arsonval type. Its internal resistance was about 1,000 ohms, and it readily indicated corresponding to a change of potential of 0.00002 volt. The galvanometer was hung upon a Julius suspension, to protect it from the annoying vibration caused by the heavy testing machines close at hand.

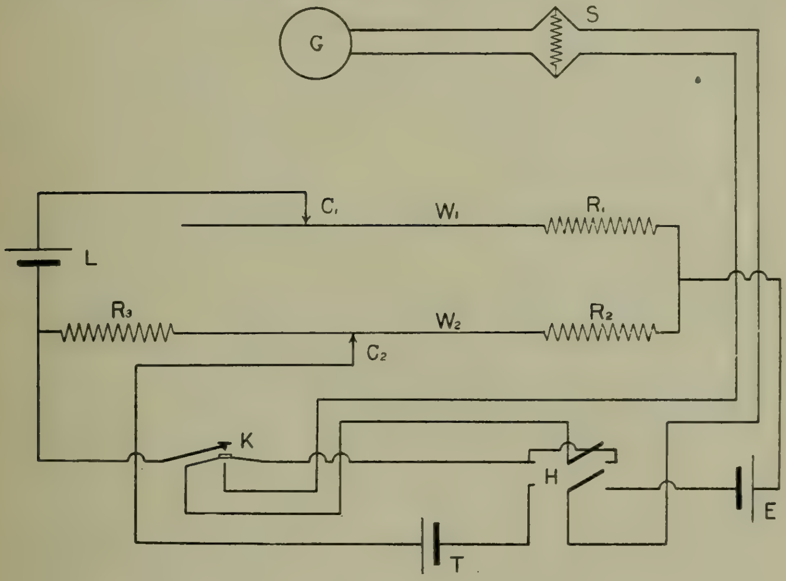

Fig. 1.

The shunt, S, was used to protect the galvanometer from too heavy currents during the preliminary adjustments of the resistances. Its resistance could be varied from a few ohms to infinity.

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[9] Physiko-Chemische Messungen, p. 361.

The specimens of iron used were made from two lots of exceptionally pure Swedish charcoal iron; one lot was of hot drawn wire about 0.25 inch in diameter; the other was of bar iron about 0.50 inch in diameter. The manipulation of specimens of this diameter is much more convenient than in the case of specimens of fine wire. The stresses can be determined more accurately. The question of inequality in the distribution of the strain over the cross-section of the specimen due to the cold flow of the metal is of no importance, because there is little cold flow of metal under the stresses which were measured, *i. e.,* below the elastic limit. The bars were cut in lengths of about 18 inches, and the central portion reduced in a lathe for a distance of about 1 inch until a zone of bright new metal was exposed. This band was smoothed in the lathe, first with a file and finally with emery cloth of moderate fineness. It is necessary to have the length of the reduced portion of the specimen at least 1 inch in the case of the ½-inch specimens, in order to eliminate the effect of the portion of larger diameter upon the strength of the reduced portion. Tests made at the Watertown Arsenal upon rolled plate indicate that the strength of the metal at the reduced section may be increased as much as 20 per cent. where the length of the reduced portion is very small. By making the reduced portion greater than twice the diameter, it is fairly certain that the condition of the metal at the center of the reduced portion is the same as it would be if the bar were of the same diameter throughout. With the exception of a narrow zone about 0.25 inch wide at the middle, the bars were covered with a waterproof coating to insulate the metal from the solution except at the desired point. A number of insulating substances were tried—rubber, wax, paraffin, and collodion, but the most satisfactory was ordinary shellac applied in two or more thick coats. The shellac is not allowed to dry perfectly hard, and so it remained sufficiently elastic to stretch with the iron. Electrical contact with the iron was made by soldering, in the case of the 0.25-inch specimens, and by means of a machine screw fitting a tapped hole in the end of the larger specimens. The form of cell was suggested by the one used by Richards and Behr. It consisted of a central tube about 3 inches long and 1 inch internal diameter, open at both ends. To this were bound, by means of adhesive tape, three smaller tubes of the same length, closed at the bottom. The bottom of the central tube was closed by a rubber stopper, carefully cleaned, through which the iron bar projected so that the reduced portion came at the middle of the tube. The central tube containing the specimen was filled with ferrous sulphate, and then the three outer tubes were filled, one with ferrous sulphate, and the other two with potassium chloride. All four tubes were then connected by means of siphons. The siphon of the normal calomel electrode dipped into the last KCl tube. These precautions were successful in preventing the diffusion of the $FeSO_4$ into the tube containing the normal electrode; not even a trace of iron was found in the latter after six weeks of constant use. The $FeSO_4$ solution was protected from air by a layer of paraffin oil carefully washed to remove traces of alkali or acid. It had been standing over very finely divided pure metallic iron in an atmosphere of hydrogen for six months, so that it was absolutely neutral.

It was found impossible to use testing machines operated by power, as the rapidly moving belts produced such a strong statical charge upon the machines as to make potential measurements quite out of the question. A testing machine operated by hand was found to be less convenient, but quite as satisfactory in every other respect.

Method of Testing.

When everything was ready for the test, the specimen was lightly rubbed with fine emery to remove traces of oxide formed while the shellac was drying, inserted in the cell, and the latter filled with ferrous sulphate and potassium chloride in the appropriate tubes. The siphons were then filled and inserted, and the specimen placed in the testing machine. The mercury electrode was then hung in place, and the cell connected in the position lettered T in the diagram of the apparatus. The sum of the resistances, R_2 and R_3, is made some convenient number, such as 75, 100, or 200 ohms, and then R_1 is adjusted until the drop in potential between the outside terminals of R_2 and R_3 is exactly equal to the potential difference of the cadmium cell; the fine adjustment of R_1 is obtained by means of the sliding contact, C_1. This measurement is made with the switch, H, closed to the right. Then the switch is thrown to the left, and the resistances R_2 and R_3 are varied (keeping the sum always the same) until the iron-mercury cell is just balanced against the storage cell, with the sliding contact, C_2, somewhere near the middle of the slide wire. Then the potential difference between the outside terminals of R_2 and R_3 is verified, and finally the slide wire reading on W_2 is recorded, as well as the resistances R_2 and R_3. Suppose the slide wire reading is *a* millimeters and the total resistance of the slide wire is *b* ohms, then the potential difference is

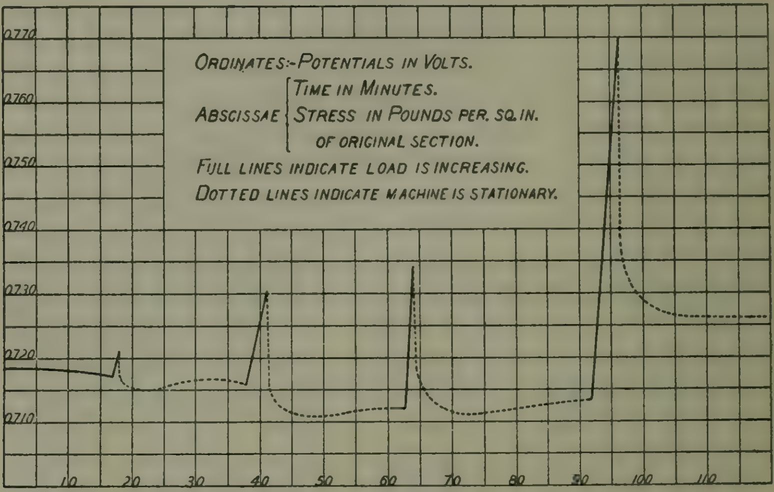

Fig. 2.

$$1.0185\left(\frac{R_3}{R_3 + b + R_2} + \frac{a \,.\, b}{1000\ (R_3 + b + R_2)}\right) \text{volts}$$

The specimen was allowed to remain in the machine at rest until the electromotive force was constant to 0.0001 volt over a period at least as long as the test would last. The initial electromotive force was always higher by several millivolts than the final constant value, probably due to an oxygen film on the surface of the metal.

The specimens were first placed under a slight load, in order that there might be no delay by reason of adjusting the wedges. A large number of pieces of iron were broken, but the results of but one typical experiment will be given. These are shown in Fig. 2. The load was put on uniformly, and the potential dropped very slowly until, at a stress of about 31,000 pounds per square inch, the electromotive force had decreased 0.9 millivolt.[10] When the machine was stopped at this point, the beam of the machine sagged, showing that the elastic limit of the piece had been passed. When stress was again applied, the potential rose suddenly 3.9 millivolts, and when the machine was stopped, it dropped to its former value in fifteen seconds, then sank more slowly to a minimum, and then started slowly to rise again. As the load was put on a second time, the character of the change was similar to the first—the same sharp rise, followed by an abrupt fall when the machine was stopped, then a slower fall, and then a rise to a constant value. The magnitude of this sudden rise depended upon the rate at which the stress was applied. A slight difference was that in the second and third loadings the sharp rise did not take place until several seconds after the loading had commenced. The final value after fracture was, in this case, about 8 millivolts higher than the initial value. In this plot time in minutes is plotted as abscissæ, because it is practically impossible to determine the actual stress when the specimen has begun to "draw out" under stress approaching the breaking stress.

The potential, after fracture, of the following six specimens was carefully noted, and when constant was measured. The original and final values, together with the differences, are:

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[10] The result of stress up to the elastic limit in seven other runs was as follows:

Mark.	Decrease in e. m. f.	Stress at which e. m. f. begins to increase.
9	0.0000	31000.
10	0.0000	29000.
11	0.0002	29000.
12	0.0000	20000.
13	0.0001	25000.
14	0.0000	30000.
15	0.0001	24600.

Mark	Material	P_1	P_2	$P_2 - P_1$
5	**Mild Steel**	0.7329	0.7310	—0.0019
6	**Swedish Iron**	0.6927	0.6993	+0.0066
10	" "	0.7117	0 7165	+0.0048
11	" "	0. 224	0.7223	—0.0001
15	" "	0.7206	0.7282	+0.0076
20	" "	0.7182	0.7259	+0.0077

These potentials are all the potentials of the whole cell, *i. e.*, Fe — $FeSO_4$ — KCl — Hg. The potential of the iron electrode alone may be found by subtracting the value of the calomel electrode, 0.5620 volts, from the values given. The results thus obtained agree with the work of Richards and Behr quite closely.

The cause of the abnormal rise observed at high stresses was next considered. Change in temperature suggested itself as the most probable cause, although iron under these conditions has been shown to have a negative temperature coefficient. In order to duplicate as nearly as possible the thermal conditions which obtain in the iron electrode, a device was used whereby there was a continual flow of heat from the electrode to the solution. A hole about ⅛ inch in diameter was drilled throughout the length of one of the electrodes. The upper end was joined by a rubber tube to a reservoir directly above, holding about 2 liters. A copper-nickel thermopile was soldered to the surface of the electrode, where it was in contact with the liquid. Copper, nickel, and solder were insulated from the solution by means of shellac. Hot water was placed in the reservoir, and allowed to flow down through the electrode; the rate of flow was regulated by means of a screw pinchcock. The potential measurements were made in the usual manner; the temperature measurements were accurate to at least 0.2° C. The result of this experiment is given in Fig. 3. It is evident that a rise of temperature produces a decided decrease of electromotive force. This experiment was repeated in the absence of the copper-nickel thermopile, which it was thought might possibly have caused the decrease in e. m. f., on account of defective insulation or other cause. Furthermore, the copper wire which had been soldered to the base of the electrode to furnish electrical contact was replaced by a pure iron wire merely twisted about the electrode. Also the water used to heat the specimen was replaced by paraffin oil. The repetition of the experiment with these precautions gave entirely concordant results. This fall of potential, due to rise in temperature, explains the fact that the dotted curves in Fig. 2 fall below the normal potential of the iron bar.

If the sudden rise in potential above the elastic limit is caused by temperature changes in the electrode, then, since iron has a negative temperature coefficient, the specimen must cool off as the breaking load is approached. Such a phenomenon, though highly improbable, is perhaps conceivable. Experiment showed, however, that there is a continuous rise in temperature from the elastic limit to the breaking load. The rise of temperature in this test was determined by means of the copper-nickel thermopile previously used. The junction was tightly bound by means of rubber bands to the reduced portion of the tension specimen. The results are shown in Fig. 4.

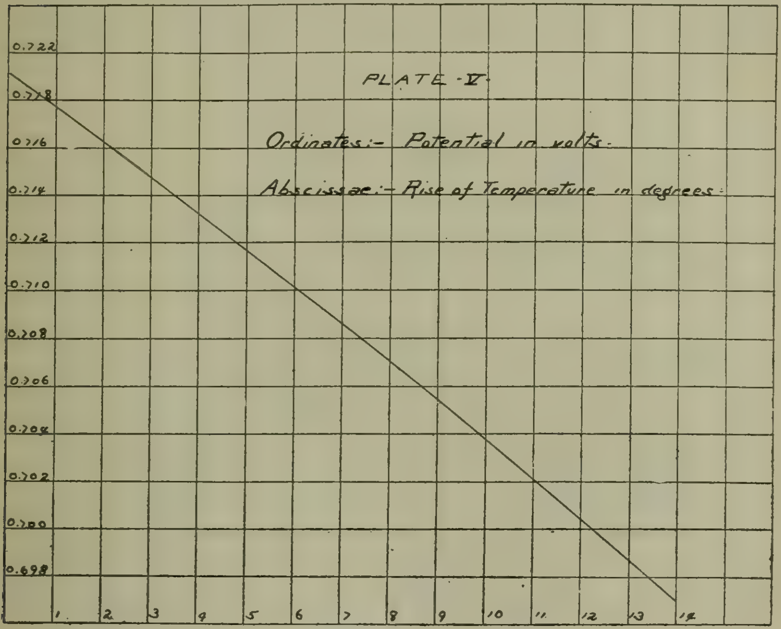


Fig. 3

An experiment was also made with normal ferric chloride as electrolyte to see if this change in potential below the elastic limit also occurred. The specimen was prepared in identically the same manner as the previous ones. Soon after immersion in the ferric chloride it became coated with bubbles of hydrogen, and the surface lost its metallic luster and grew black. The potential rose rapidly during the first and second days. On the third and fourth days the potential was not measured. On the fifth day it had risen from 0.5279 volt to 0.6638 volt, and was very constant. Scraping the specimen by means of a sharpened wire produced a decrease of 0.0031 volt. The next day (the sixth) the bar was pulled nearly to fracture. The potential decreased gradually 0.0006 volt from 1,200 pounds stress per square inch to 32,600 pounds—the yield point. Here the potential rose, as in all previous cases, but the subsequent behavior was irregular. This experiment confirms the previous ones with ferrous sulphate as electrolyte, and makes it still more probable that the variations in potential below the elastic limit, observed by Hambuechen, were caused by something other than stress.

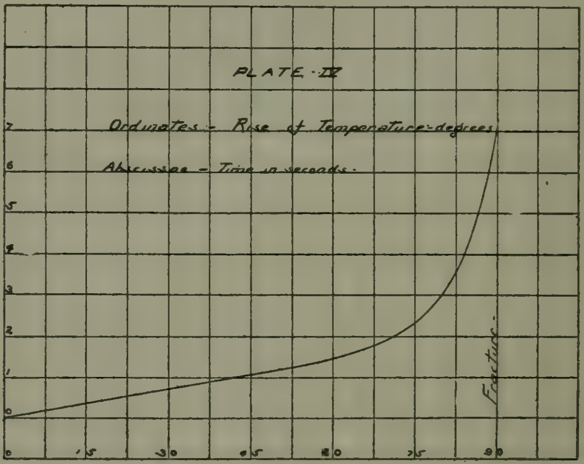


Fig. 4.

If there is a permanent difference in electromotive force between a strained and an unstrained piece of metal, it should be apparent in the case of hard-drawn wire when compared with the same wire annealed. A number of samples of steel wire in its strained condition were obtained, and portions of each sample carefully annealed in a vacuum. In almost every case a difference of potential was observed between the annealed and the unannealed specimen. But further investigation showed that as great, and frequently greater, differences existed between the different portions of the *same wire*, both in the strained and in the annealed condition. This observation will form the basis of a subsequent communication.

Summary.

The results of the foregoing experiments may be summarized as follows:

1. The magnitude of the potential changes suffered by soft iron when tested in a tension machine below the elastic limit is exceedingly small. In the majority of cases it was less than 0.0001 volt. The maximum change was 0.0004 volt.

2. The change, when great enough to be measured, was negative, *i. e.,* the strained metal had a slightly lower potential than the same metal unstrained.

3. Somewhere above the elastic limit the potential rises suddenly several hundredths of a volt. The magnitude of the increase depends upon the rate of straining, and ceases abruptly when the straining ceases.

4. Measurements upon specimens under torsional stress give results similar to those obtained from tension tests.

5. Out of a considerable number of specimens strained to breaking, the potential of six reached a constant value shortly after fracture. The difference between the initial and final potentials varied from —0.0019 volt to +0.0077 volt, and the single potential of unstrained iron was found to be 0.156 volt.

Research Laboratory of Technical Chemistry,
Massachusetts Institute of Technology, June, 1907.

DISCUSSION.

Prof Jos. W. Richards: I think the explanation of this rise in e. m. f., when a specimen has passed its elastic limit, is undoubtedly due to the heating of the piece by the work which is done upon it when it is strained; the temporary heating of the piece changes the temperature conditions and raises the e. m. f. That is confirmed by the fact, stated by Dr. Walker, that the more rapidly you strain it, the more quickly it rises; and then the e. m. f. falls rapidly, which is due to the cooling of the piece.

Mr. W. H. Walker: When you heat the piece by other means the electromotive force falls, not rises. The iron has a negative thermal coefficient. I think we have proven conclusively that it is not a heat effect which produces the rise in electromotive force.

Mr. E. P. Schoch: I believe that you will find that if the surface is very carefully ground, the potential is much higher. What is the maximum potential you obtained when the piece broke?

Mr. Walker: About 35 to 40 millivolts higher.

Mr. W. R. Mott: Neumann's value of the single potential of iorn in ferrous solution was +0.087 volt, where the potential of the normal electrode was taken as —0.56 volt. This compares badly with values calculated in the paper, "Single Potentials of the Halogen Elements," (Trans. Amer. Electrochem. Soc. V, p. 74). The calculated single potential of iron in ferrous solution was +0.18 volt. T. W. Richards and Behr give the potentials of iron in ferrous solutions between +0.16 and +0.19 volt. When the iron is prepared very pure and fused in a vacuum, then the potential is +0.15 volt; Mr. Walker has exactly confirmed these high values, which are very interesting because they closely check each other and the values calculated from thermal data.

A paper read at the Eleventh General Meeting of the American Electrochemical Society, in Philadelphia, Pa., May 2, 1907; President Carl Hering in the chair.

CHANGES OF CONCENTRATION AND MIGRATION VELOCITIES.

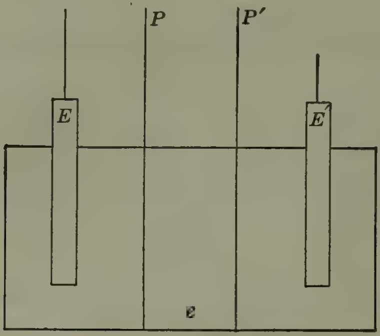
By C. J. Reed.

According to the theory of electrolytic dissociation, the changes in concentration produced in an electrolyte by electrolysis are caused by the migration of positive and negative ions in opposite directions with constant, but unequal velocities. I am not aware that any proof of this conclusion has ever been published, and have never been able to obtain any proof from the advocates of the theory. The statement that "changes in concentration are caused by unequal migration velocities of the oppositely charged ions" is the nearest approach to proof that I have been able to obtain.

Some writers have published explanatory diagrams, graphically representing a certain number of positive and negative ions, with an explanation of the manner in which, according to their ideas, the unequal velocities in opposite directions might produce an increased concentration at one electrode and a diminished concentration at the other. But these diagrams and explanations have in all cases involved assumptions which are contrary to the facts, and which render the explanations, not only inadequate, but untenable.

From an examination of the facts, it may be shown that the so-called migration of oppositely charged ions, with constant, but unequal velocities would not only cause no change in concentration, but really could not occur.

In the accompanying diagram, let E and E' represent the electrodes of an electrochemical cell immersed in an electrolyte, e. It is assumed that the electrodes remain fixed in position, and that the electrolyte is of uniform concentration. Let us assume that the electrolyte contains negatively charged ions, which migrate from E towards E' with a constant velocity v; and positively charged ions, which migrate from E' towards E with a constant velocity $n\ v$, in which n may be any constant. Let us consider a portion of the electrolyte included between any two arbitrary fixed planes, P and P', which are at finite distances from the electrodes.



It is admitted that the number of positive ions between these planes is at all times equal to the number of negative ions, that is, that there are no "unsaturated" ions present in this space. Let us assume that during a certain interval of time one negative ion crosses the plane, P, into the space between the planes. During the same time n positive ions will leave this space by crossing the plane, P, in the opposite direction. But, since the respective velocities of the positive and negative ions are by hypothesis uniform and constant, it follows that during the same interval one negative ion must leave the space by crossing P', and n positive ions must enter the space by crossing P'. Constancy of chemical composition also necessitates this.

It follows that the space between P and P' must contain, in its final state, the same number of ions of both kinds as in the initial state. The average concentration, therefore, between the planes is the same in the initial and final states. This will be true whatever may be the distance between the planes, and will be true of the spaces between any number of planes that may be assumed. It will also be true whether the planes be parallel or not.

If, therefore, the entire electrolyte included between the electrodes be divided up by an indefinite number of planes, the average concentration in each of the spaces so produced will be the same in the initial and final states. But in the initial state the concentration is by hypothesis the same in all of the spaces..

It is, therefore, the same in all of the spaces in the final state. As no change in concentration can be produced in an arbitrarily assumed short interval of time, none could be produced by any number of such intervals.

The same reasoning will apply also to an electrolyte which, in the initial state, is not of uniform concentration.

Furthermore, it follows, that, since no changes in concentration could be produced in the body of an electrolyte by an inequality in the constant velocities of the oppositely moving ions, there would be as a result of such inequality, accumulations of oppositely charged ions at the two electrodes, which would be proportional to their velocities. This would be contrary to Faraday's law and contrary to the facts.

The assumption of unequal constant velocities is, therefore, not only incompetent to explain changes in concentration, but is a direct contradiction of the most thoroughly established facts of electrochemistry.

DISCUSSION.

PRESIDENT HERING: The question arises in my mind, has it not been found that such changes do occur, and that the explanation of the difference of migration velocities was offered to explain something which had been observed? Another matter that comes up in my mind is that Mr. Reed has not considered a diaphragm. He considers a parallel plane, but that is a little different thing from considering a diaphragm. There may be such a thing as a solution going through a diaphragm more freely in one direction than in the other. Such things as that are known to exist.

MR. C. J. REED: I do not think there is anything in the paper denying the fact that there are changes of concentration produced in electrochemical action, but the theory of oppositely-charged ions migrating in opposite directions with unequal velocities will not account for those changes. That is all that I expected to show in the paper, and one is at liberty to accept either the facts or the theory.

President Hering: Is there no one here to defend the other side?

Dr. E. F. Roeber: There is no doubt that Mr. Reed's argument as to the constancy of concentration between the two planes, P and P′, is absolutely sound. No one has ever thought differently. But his argument does not apply to the spaces between P and the electrode E and to the other space between P′ and the electrode E′. It is there where the concentration changes are observed, and are accounted for by the model or picture of migrating ions of various velocities.

Mr. Reed: Whatever is true of the space between P and P′ will be true of another similar space and of any number of such spaces into which the electrolyte may be conceived to be divided, regardless of the sizes or number of those spaces. Now let us assume those spaces to be infinitesimal in size and to occupy the entire space between the electrodes; then it will be seen, I think, that no change in the concentration can be produced in the electrolyte, except in the space which is at an infinitesimal distance from the electrode. That would be less than a molecular distance. What I wanted to show was that this theory would not explain the changes of concentration which take place in the body of the electrolyte.

Mr. W. R. Mott: I recall a question that Dr. Kahlenberg asked his class once in physical chemistry, and it is this: "If we had, in place of the electrolytic deposition, a chemical means for removing the products as they occur, would we have the same concentration changes?"

Prof. J. W. Richards: Without being able to answer that question, I would say that I have often put that query to my own class, and answered it with the statement of my belief that we would. I have never been able to prove it.

Mr. Reed: There is no question but that the actual operation of the variation in concentration about the electrodes is very greatly influenced by the products which are formed at the electrodes and which diffuse, or are conveyed by gravity or other means into other parts of the electrolyte; but those are questions with which I am not at all concerned in this paper.

A paper read by Dr. W. D. Bancroft at the Eleventh General Meeting of the American Electrochemical Society, in Philadelphia, Pa., May 2, 1907; President Carl Hering in the chair.

POLARIZATION VOLTAGES OF SILVER NITRATE SOLUTIONS.

By J. A. Wilkinson and H. W. Gillett.

Some qualitative experiments having shown that the decomposition voltage for acidified silver nitrate solutions varied with the concentration of the acid, experiments were made to determine the various factors. The electrodes consisted of two smooth, stiff platinum electrodes, each having a surface of 14.64 cm². These were placed 3 cm. apart in a beaker, which required 150 cc. of solution to fill it to the upper edge of the electrodes. This same amount of solution was used in each case. Instead of determining the decomposition voltage, or point at which the current begins to increase beyond the residual current, it was found better to measure the polarization voltage, or counter-electromotive force given by the cell after it had been polarized by a charging current. To do this, the charging circuit was broken and the cell short-circuited on a high-resistance voltmeter. Readings were taken every quarter minute and plotted with voltages and time as the co-ordinates. The horizontal portion of the curve is taken as the polarization voltage. In cases where there is no good horizontal portion, the apparent inversion point of the curve was taken.

Table I.

Temperature 18.5°
3.75 g. $AgNO_3$ and 7 g. HNO_3 per 150 cc.
Voltage readings every quarter minute.

1.08	1.02	1.015	0.84	0.27	0.16
1.05	1.02	1.01	0.75	0.25	0.15
1.04	1.02	1.01	0.67	0.24	0.14
1.03	1.02	1.00	0.59	0.22	0.14
1.025	1.02	1.00	0.51	0.21	0.13
1.02	1.02	0.99	0.40	0.20	0.13
1.02	1.02	0.97	0.35	0.19	0.12
1.02	1.02	0.94	0.32	0.18	0.12
1.02	1.015	0.90	0.37	0.16	0.11

In Table I is given a good example. The charging current was 6.5 milliampères for 1.25 minutes, and the polarization voltage is clearly 1.02 volts.

The polarization voltage, as thus determined, is identical with the decomposition voltage when the reaction is reversible. When there is no acid at all in the solution, the readings were not congruent. When there is a large amount of acid in the solution, or when the temperature is high, it is hard to get a satisfactory polarization voltage, because the chemical action is increased and the deposit dissolves too quickly. The charging or polarization current was varied to meet the exigencies of each particular case, being larger when the concentration of acid, or when the temperature was high. When difficulties were encountered, readings were taken every five seconds. In every case the observations were checked by repeating them under the same conditions. A calibration curve for the Weston voltmeter was obtained by checking against a standard one belonging to the Department of Physics.

There are four variables to be considered: temperature, silver nitrate, acid, and water. In our experiments, we have let each one of these vary by itself, keeping the other three constant. Thus, keeping the acid, water and silver nitrate constant, we varied the temperature. Keeping the temperature and the ratio of acid to water constant, we varied the concentration of the silver nitrate. Keeping the temperature and the ratio of silver nitrate to water constant, we varied the concentration of the acid. Keeping the temperature and the ratio of acid to silver nitrate constant, we varied the concentration of the water. In this way a pretty fair idea can be obtained of the effect due to each of the variables, although it was not attempted to make the treatment exhaustive. The silver nitrate was from the stock-room and was not purified further. The acid was so-called, pure, concentrated nitric acid from the stock-room, and its specific gravity was 1.41.

In Table II are two runs to show effect of temperature.

TABLE II.

EFFECT OF TEMPERATURE.

Solution A=3.75 g. $AgNO_3$ + 0.7 g. HNO_3 per 150 cc.

Temp.	Volts	Temp.	Volts	Temp.	Volts.
14°	0.89	46.5°	0.928	68°	0.948
20	0.89	55	0.928	70	0.953
32	0.91	66	0.938		

Solution B=11.296 g. $AgNO_3$ + 2.80 g. HNO_3 per 150 cc.

Temp.	Volts	Temp.	Volts	Temp.	Volts
0°	0.91	20°	0.924	39.5°	0.938
11.5	0.913	27	0.928	50	0.944
15	0.918	31	0.929	61	0.952

When these results are plotted it is seen that the data for solution B lie fairly accurately on a straight line, while those for solution A vary irregularly from a straight line parallel to that for solution B. We may, therefore, consider the temperature co-efficient as approximately linear over this range of temperatures and concentrations. The value of the temperature co-efficient is approximately + 0.0008 volts per degree.

In the next series, the concentration of the silver nitrate was the only variable. A solution of 10 cc. HNO_3 and 990 cc. H_2O was made up, and varying amounts of $AgNO_3$ were dissolved in 150 cc. portions. No corrections were made for expansion or contraction when the silver nitrate dissolved. There was a fluctuation of temperature between the first three and the last five observations; but this change of one degree means a correction of less than one millivolt. The data are given in Table III, and are shown graphically in Fig. 1.

The polarization voltage increases with decreasing concentration, but is not a linear function. By extrapolation to zero concentration of silver nitrate, an apparent value of about 1.06 volts is obtained. Or course, there is no certainty that this extrapolation is justified, but it does not seem an improbable value. The change of 0.13 volts, while the silver nitrate concentration varies in the ratio of 1 : 55, is unexpectedly large.

TABLE III.

EFFECT OF SILVER NITRATE.

g. $AgNO_3$ per 150 cc.	g. HNO_3 per 150 cc.	Volts	Temp.
5.4733	1.05	0.91	23°
2.9230	1.05	0.927	23
1.9281	1.05	0.948	23
1.0687	1.05	0.967	24
0.6227	1.05	0.985	24
0.4270	1.05	1.005	24
0.2010	1.05	1.025	24
0.1000	1.05	1.040	24

In Table IV are the data obtained when nitric acid was the variable. A correction for temperature must be applied before the results are strictly comparable. The results are shown graphically in Fig. 2.

TABLE IV.

EFFECT OF HNO_3

3 g. $AgNO_3$ per 150 cc.

g. HNO_3 per 150 cc.	Volts	Temp.	g. HNO_3 per 150 cc.	Volts	Temp.
0.14	0.818	25°	2.24	0.986	19.5°
0.28	0.861	25	2.80	0.995	21
0.42	0.915	25	3.08	1.005	20
0.84	0.927	25	3.36	1.005	20
1.12	0.947	25	3.64	1.015	20
1.36	0.948	19.5	4.20	1.025	21
1.40	0.952	25	4.90	1.033	21
1.68	0.965	20	6.16	1.034	25
1.82	0.966	25	7.70	1.044	21
1.96	0.972	19.5	10.50	1.058	21
2.16	0.981	20			

Increasing the nitric acid concentration increases the polarization voltage, at first very much, but afterwards less. With no nitric acid this concentration of silver nitrate gives a polarization voltage of about 0.65. Addition of 0.14 g. HNO_3 per 150 cc. raises the value to 0.818, and, apparently, causes the formation of the peroxide or peroxynitrate at the anode. The increase in concentration from 0.14 g. HNO_3 to 10.5 g. raises the polarization voltage by 0.24 volts.

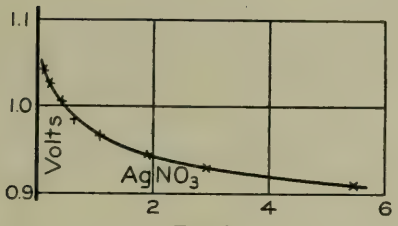


FIG. 1.

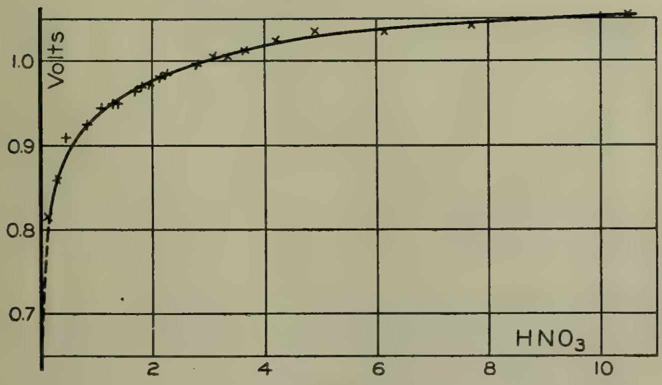
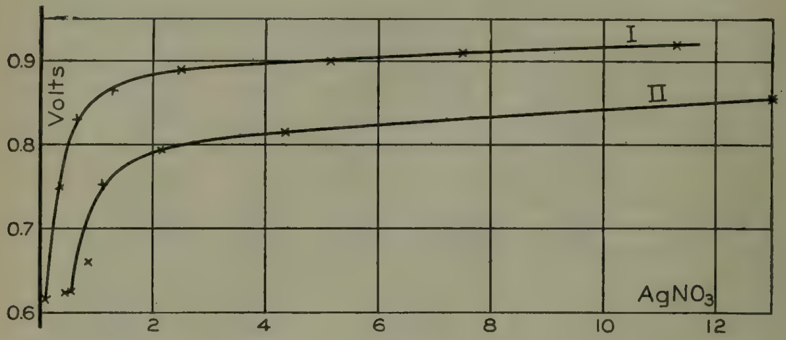
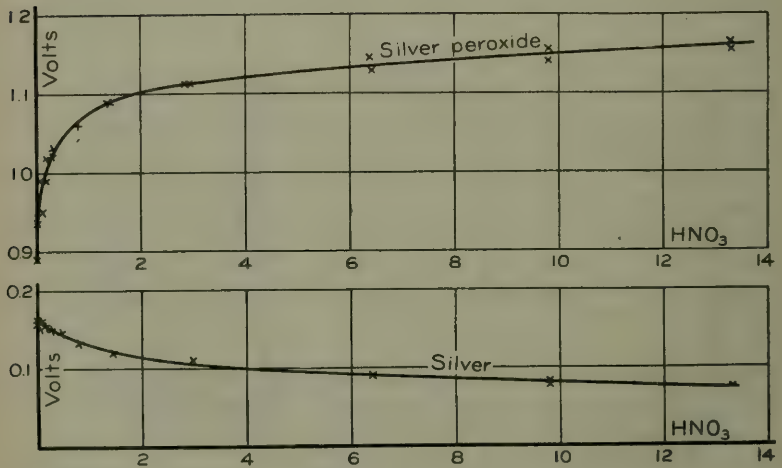


FIG. 2.



Volts
0.9
0.8
0.7
0.6
I
II
AgNO$_3$
2
4
6
8
10
12

FIG. 3.



Volts
1.2
1.1
1.0
0.9
Silver peroxide
HNO$_3$
2
4
6
8
10
12
14
0.2
0.1
Volts
Silver
HNO$_3$
2
4
6
8
10
12
14

FIG. 4.

In the experiments to determine the effect of water as a variable, the ratio of acid to silver nitrate was kept constant. The results are given in Table V, and in Fig. 3.

TABLE V.

EFFECT OF WATER.

g. $AgNO_3$ per 150 cc	g. HNO_3 per 150 cc.	Volts	Temp.
Ratio of $AgNO_3$ to $HNO_3 = 4.13$			
11.29	2.735	0.924	20°
7.527	1.823	0.91	20
5.090	1.234	0.90	22
2.545	0.617	0.89	22.5
1.273	0.308	0.866	24
0.636	0.154	0.832	24.
0.318	0.077	0.745	24.5
0.159	0.038	0.620	25.5
Ratio of $AgNO_3$ to $HNO_3 = 18.7$			
13.030	0.700	0.851	21
4.340	0.233	0.817	21
2.170	0.116	0.793	21
1.085	0.058	0.755	21
0.870	0.046	0.675	24
0.543	0.029	0.630	24
0.435	0.023	0.639	24

With increasing dilution, the values for the polarization voltage fall off slowly at first, but decrease very rapidly for the very dilute solutions. It is not clear what would be the significance of an extrapolation to infinite dilution. It must also be kept in mind that the product formed at the anode probably changes when the polarization voltage falls distinctly below 0.8 volts, though this is not a point on which we have any evidence to offer.

From the last three tables we see that the polarization voltage rises when the concentration of silver nitrate decreases, and that of nitric acid remains constant; that it falls when the concentration of nitric acid decreases and that of silver nitrate remains constant; and that it falls when the concentrations of silver nitrate and nitric acid decrease in the same ratio. Owing to the marked effect thus due to the nitric acid, a few experiments were made to determine the effect of nitric acid at each electrode.

The same two platinum electrodes and the acidified silver nitrate solution were placed inside a porous cup, which dipped into a beaker containing H_2SO_4 (1 : 5), Hg_2SO_4, Hg. The porous cup had previously been boiled out with a potassium nitrate solution to prevent the precipitation of silver sulphate in the pores. The mercurous sulphate was prepared by the method of Hulett[1]. The connections were so arranged that it was possible to polarize the platinum electrodes and then to connect either one of them through the voltmeter with the mercury electrode. Using a voltmeter, one measures potential differences instead of electromotive forces; but this is immaterial so far as studying the relative effect of acid on the two polarized electrodes.

The mercury electrode is the anode in all cases. The data are given in Table VI, and are plotted in Fig. 4.

TABLE VI.

Temp.	g $AgNO_3$ per 150 cc.	g. HNO_3 per 150 cc.	Volts Hg-Ag	Volts Hg-peroxide
19°	3.00	0.00	0.16	0.89
20	“	0.07	0.16	0.948
20	“	0.14	0.15	0.987
20	“	0.28	0.145	1.015
20	“	0.42	0.14+	1.035
20	“	0.77	0.135	1.055
20.5	“	1.47	0.12	1.09
21	“	2.94	0.115	1.107
22	“	6.37	0.085	1.148
23	“	9.80	0.08	1.154
24	“	13.3	0.06+	1.16
19	3.00	0.00	0.155	0.933
22	“	0.07	0.15	0.987
22	“	0.135	0.145	1.015
22	“	0.28	0.14	1.03
22.5	“	0.49	0.135	1.045
22.5	“	0.77	0.125	1.058
22.5	“	1.47	0.12	1.078
23	“	2.80	0.105	1.098
24.5	“	6.30	0.08	1.120
25	“	9.80	0.07+	1.135
26	“	13.3	0.06+	1.150

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[1] Trans. Am. Electrochem. Soc. *6,* 109 (1904).

From Table VI it is clear that addition of nitric acid decreases slightly the potential difference between silver and the electrolyte, and increases largely the potential difference between the peroxide electrode and the electrolyte. The result is not what one might have expected. The addition of nitric acid might reasonably have been expected to force back the dissociation of silver nitrate to some extent and thus to have increased the potential difference. On the other hand, it must be remembered that the addition of nitric acid has an effect on the potential difference between the solutions. If we ignore the potassium sulphate in the walls of the porous cup and the silver nitrate in the cathode chamber, the effect due to the nitric acid is of the same general order as that required by Nernst's formula.

It is an interesting question whether one is justified in assuming that the solution pressure of silver in aqueous silver nitrate is the same as in that of a solution of silver nitrate in aqueous nitric acid. Kahlenberg[1] has shown that the addition of pyridine to aqueous silver nitrate changes the solution pressure. Pyridine is an organic liquid, miscible in all proportions with water. Nitric acid is an inorganic liquid, miscible in all proportions with water. It would be very interesting—though entirely outside the scope of these experiments—to determine the so-called single potentials for silver and silver nitrate in a solvent varying continuously from pure water to practically pure nitric acid.

The effect of acid at the peroxide electrode is qualitatively what one would expect. It is impossible to discuss the quantitative side until more is known about the real composition of what is called silver peroxide.

The general results are as follows:

1. The polarization voltage of acidified silver nitrate solutions may be made to vary from 0.625 volts to 1.05 volts.
2. The polarization voltage varies with variations of temperature, silver nitrate, nitric acid, and water.
3. The temperature coefficient is approximately 0.8 millivolts per degree over a fair range of compositions and temperatures.
4. A decrease in the concentration of silver nitrate increases the

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[1] Jour. Phys. Chem., *3*, 403 (1899).

polarization voltage if the concentration of nitric acid be kept constant.

5. A decrease in the concentration of nitric acid decreases the polarization voltage if the concentration of silver nitrate be kept constant.
6. The polarization voltage decreases if the concentration of silver nitrate and nitric acid are decreased in the same ratio.
7. When measured against a sulphuric acid, mercurous sulphate, mercury electrode, the potential difference between silver and the electrolyte is decreased slightly by the addition of nitric acid, while the potential difference between peroxide and electrolyte is apparently increased a great deal.
8. The abnormal result with the silver electrode may be due to a change in the potential difference between the solutions.
9. There is nothing in the data obtained to show whether or when the product formed at the anode changes from peroxide to oxygen.

This work was suggested by Professor Bancroft and has been carried on under his supervision.

Cornell University.

A paper read at the Eleventh General Meeting of the American Electrochemical Society, in Philadelphia, Pa., May 2, 1907; President Carl Hering in the chair.

ELECTROLYTIC PICKLING OF STEEL.

By C. J. Reed.

One of the earliest electrochemical generalizations was the general law that metals are dissolved at the anode and deposited at the cathode. There is another law equally universal which has not received recognition as such, but which, in my opinion, is no less important. It is that *higher oxides are dissolved at the cathode and deposited at the anode.*

Although this law has not received recognition as such, many instances illustrating it are of the commonest occurrence. For example, in the lead accumulator we have the deposition of PbO_2 on the anode in charging, and its conversion into $PbSO_4$ on discharging. It may be argued that in this case it is not a dissolving or depositing, but only a conversion. The same may be said of the change occurring when CuO is reduced to Cu in an alkaline electrolyte, but that does not make it an exception to the general rule that metals are deposited at the cathode and dissolved at the anode. The fact that copper oxide happens to be practically insoluble in the alkaline medium, and that $PbSO_4$ happens to be practically insoluble in sulphuric acid, does not affect the general principle involved. These are merely exceptions, due to the accidental chemical insolubility, not to electrochemical insolubility. If we substitute HNO_3, or any other acid forming a soluble salt, for the H_2SO_4, in the case of lead the peroxide is dissolved into the solution at the cathode, and deposited from solution at the anode. It is only necessary to remember, then, that an exception of the kind above noted to either of these laws occurs whenever the product formed would be insoluble in the electrolyte. While neither of these laws is strictly general, one is probably as general as the other. Of course, the law for higher oxides can only be true when the elements in question form higher oxides. Lead, sulphur, manganese, cobalt, nickel, iron, sulphur, selenium, tellurium, chlorine, bromine, iodine, nitrogen, arsenic, antimony, bismuth, tin, zinc,[1] and many other elements, form one or more higher oxides, which can be deposited at the anode and dissolved at the cathode.

The case to which I wish to call attention to-day, on account of its possible commercial utility, is the dissolving of Fe_3O_4 in H_2SO_4. This oxide constitutes the black scale, or fire-scale, formed when red-hot iron is exposed to the air. At low temperature, and in dilute solution, this scale is dissolved at the cathode, only very slowly, and if the current density is low, the iron beneath the scale will be dissolved chemically, as in the ordinary process of pickling. If, however, the temperature be maintained at about 60° C., the solution at an acid density of about 1.25, and the current density at about 70 amperes per square foot, the solvent action on the scale becomes very rapid, and the chemical action on the metallic iron is entirely prevented. Under these conditions, the removal of the heaviest scale is accomplished in from two to three minutes, and lighter scales in a correspondingly less time.

As no iron is dissolved, this method effects a great saving in two ways, by a reduction in the quantity of acid used to that required for the solution of scale alone, and by the saving of all the metallic iron necessarily dissolved in the ordinary process. In the ordinary process, the acid dissolves principally the metallic iron, and the scale is largely removed mechanically by the hydrogen gas formed under the scale. In the electric cathode process, none of the scale is removed mechanically, as no gas is formed, except by the current, and none at all under the scale.

The process may be made to generate its own sulphuric acid, by simply supplying SO_2 at the anode, which can be produced by burning pyrites or sulphur at a cost much less than that of sulphuric acid. The process, if applied to the pickling of steel wire, could be made to effect a saving of 50 to 75 cents per ton, or on the output of a single company in this country, $2,000 to $3,000 per day.

Another possible advantage would be the saving of the ferrous sulphate, which, by the ordinary process, is not worth the cost

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[1] A peroxide of zinc has been deposited by the author and will be described later.

of evaporating the dilute solution. In the electric cathode process, when the solution becomes loaded with sulphate, it requires only to be cooled, when the bulk of the sulphate is precipitated as crystals, and the solution is ready to be used over again.

In the application of the process to the pickling of wire in coils, we meet with an electrical difficulty which has not yet been satisfactorily overcome. This is the difficulty of making electrical contact with the interior of the coil. The resistance of the wire is too great for conduction along the wire, and electrical contact of adjacent coils is not sufficient. The best method would be to unwind the wire, and pass it lengthwise through the bath, but this is objected to by operators of wire mills.

I have here a sample showing the pickling. It consists of four pieces of iron; one was subjected 20 seconds; one, 40; one, 80 seconds, and the other for 2 minutes.

DISCUSSION.

MR. C. F. BURGESS: There are various interesting peculiarities in the action of an acid on a metal, when that metal constitutes the cathode. We ordinarily think of an acid of a given strength as being capable of dissolving a metal at a certain rate. If, while this corrosion is taking place current flows to the metal as a cathode, we naturally expect it to dissolve at a lesser rate, as Mr. Reed explains in his paper, but there are many cases, depending upon the strength and composition of the acid, in which the chemical corrosion is actually increased by the cathode current, rather than diminished. Just what that is caused by I would not attempt to say, but I hope to again refer to it when a large amount of data which has been obtained may be classified.

DR. C. A. DOREMUS: Within recent years hydrofluoric acid has been used in pickling iron (Stahl, K. F., J. Am. Chem. Soc., XVIII, 425, 1906). Has Mr. Reed made any experiments with that acid aided by the electric current?

MR. C. J. REED: It removes siliceous scale.

DR. DOREMUS: It also removes the iron scale; a weak hydrofluoric acid removes rust stains on linen without damaging the linen. The acid acts on the oxides of iron more readily, apparently, than it does on the metal. I didn't know whether you had made any experiments in that regard. It is very cheap, being used now very largely by the ton.

MR. REED: Hydrofluoric acid has been used in pickling cast iron to a great extent; it is advantageous for that purpose, because of the siliceous nature of the scale; but what is called "fire-scale" is easily removed by any acid which will generate hydrogen in connection with the iron, either by the ordinary process of soaking or by the cathode process. But to use the electric current with hydrofluoric acid, I think, would be objectionable, and even to use hydrochloric acid would generate free chlorine.

MR. W. R. MOTT: There would be no free fluorine, practically, and you would have oxygen or ozone. The action of fluorine would give about 20 per cent. ozone.

MR. H. HOWARD: Have you, Mr. Reed, tried this process on a large scale.

MR. REED: I have not tried it on a scale of any extent.

A paper read at the Eleventh General Meeting of the American Electrochemical Society, in Philadelphia, Pa., May 3, 1907; President Carl Hering in the chair.

THE WORK DONE IN ELECTROLYSIS.

By Joseph W. Richards.

The object of the following experiments was to try to determine, in a limited number of cases, the proportion of the electrical energy absorbed by an electrolytic cell which appeared as heat, and the proportion disappearing, or becoming latent, in doing chemical work. For instance, when dilute sulphuric acid is in course of regular decomposition into oxygen and hydrogen, with platinum electrodes, what proportion of the energy of the current disappears in doing chemical work, the work of decomposition?

The energy disappearing in doing chemical work can be determined by measuring the total energy of current used by the cell (in volt-ampere-seconds, or joules) and determining the heat set free calorimetrically by the rise in temperature of the cell. Knowing the water value of the electrolyte and electrodes, and that of the containing vessel, it is possible to measure the heat actually developed in the cell. The water value of the containing vessel can also be determined experimentally, which is a better method than multiplying its weight by its specific heat, since the loss by radiation and conduction away from the vessel, for the duration of an experiment, can be determined and subsequently allowed for.

The Apparatus.

In these experiments, a cell was arranged, consisting of a rectangular vessel of 500 c.c. capacity, placed inside a larger jar of 2,000 c.c. capacity, and the space between filled with cotton wadding. To ensure constant external conditions, the whole was placed inside the water-jacket of a Berthelot calorimeter, so that it was protected from drafts and changeable external radiation. A Beckman thermometer passed through a slit in the pasteboard cover, and served also as an efficient stirring rod. A Gülcher thermopile furnished a very steady electromotive force, and the current was measured by a shunt ammeter, and a voltmeter attached directly to the electrodes, both being standard Weston instruments.

Heat Lost to the Vessel.

To determine what proportion of the heat generated in the cell was lost to the containing vessel, and what was found by the thermometer, the cell was filled with 400 c.c. of copper sulphate solution of the formula $CuSO_4.200H_2O$, of specific gravity 1.042, and containing 4.2 per cent. of $CuSO_4$. The specific heat of this solution, at 25° C., is 0.951 (Marignac). Two clean copper sheets were used as electrodes, weighing 95 grams, and two brass binding screws were used, weighing 60 grams. The water value of solution, electrodes and clips was 405.5 grams. By passing measured currents through this cell, and noting the rise of temperature produced in a given time, the proportion of the heat energy developed in the cell, which was found by the thermometer, could be obtained. An example of such a test is as follows:

Time	t	Volts	Amperes	Watts	= Cal. in 5′
5.40	3.563				
.45	3.500	3.36	0.300	1.008	72.5
.50	3.571	2.40	0.212	0.509	36.5
.55	3.581				
6.00	3.520				

The temperature changes are:

5.40 — 5.45	current off	— 0.063
5.45 — 5.50	current on	+ 0.071
	Net gain from current	+ 0.134
5.50 — 5.55	current on	+ 0.010
5.55 — 6.00	current off	— 0.061
	Net gain from current	+ 0.071

In these cases, we have, respectively:

Thermal value of current	72.5 cal.	36.5 cal.
Rise of Thermometer	0.134°	0.071°
Heat received by bath and electrodes	54.3 cal.	28.8 cal.
Proportion of total thus found . . .	75 per cent.	78.9 per cent.

A considerable number of tests with varying currents showed from 75 to 82.4 per cent. of the total heat of the current thus accounted for, the average value of all being 78.8 per cent., leaving 21.2 per cent. as absorbed by the containing vessel.

With this datum found, the cell was arranged for doing decomposition, as follows:

Decomposition of Water.

A solution of $H_2SO_4.200H_2O$ was taken, containing 2.2 per cent. H_2SO_4, specific gravity, 1.015, specific heat, 0.9747 (Marignac). Four hundred c.c. of this occupied the cell, with platinum electrodes, the whole having a water value (exclusive of the containing vessel) of 395.7 grams. On sending current through this cell, the volts and amperes were read, and thus the total energy of the current was known, the rise of temperature was taken, and the product of this into the water value, 395.7, assumed to be 78.8 per cent. of the total heat developed. The difference gives the heat disappearing as chemical energy, and thence the proportion of the total thus used is obtained. This proportion of the total voltage used gives the voltage disappearing as chemical work. An actual example will best illustrate the experiment:

Time	t	Rise	Volts	Amperes	Watts	= Grm. cal. in 5′
2.20	0.890	0.015				
.25	0 905					
.30	1.155	0.250	3.73	0.789	2.95	211.7

Net rise = 0.235 . Calories found 395.7 × 0.235 = 93.0

" developed 93.0 ÷ 0 788 = 118.0

" lost as chemical work = 93.7

Proportion of voltage represented by the calories lost

$$\frac{93\ 7}{211.7} \times 3{\cdot}73 = \underline{1.65}$$

Similar tests, carefully made, gave, in four cases, 1.55, 1.58, 1.65 and 1.68 volts, disappearing as chemical work, an average of 1.61. These were made at the end of a series of some 30 tests, which gave varying results, from one cause or another, but several evident sources of error were progressively eliminated, and this set of four represent the best result so far reached. It is intended to continue these tests, using different electrodes, and with other solutions, in order to determine, if possible, to 0.01 volt the actual absorption of e. m. f. when setting free hydrogen and oxygen.

Similar tests were made with $CuSO_4.200H_2O$ solution, using a copper cathode and a platinum anode. The experimental figures are:

Time	t	Rise	Volts	Amperes	Watts	Cal. in 5′
8.55	2.339	— 0.008				
9.00	2.331	+ 0.088	4.48	0.233	1.045	74.9
9.05	2.419	+ 0.091	4.47	0.237	1.059	76.0
9.10	2.510	— 0.007				
9.15	2.507					

Net rise, 0.096° in first period and 0.098 in second; calories found as sensible heat:

$$401.3 \times 0.096 \div 0.788 \doteq 48.9 \text{ cal.}$$
$$401.3 \times 0.098 \div 0.788 = 49.9 \text{ ''}$$

Calories lost as doing chemical work, in each period:

$$74.9 - 48.9 = 26.0 \text{ cal.}$$
$$76.0 - 49.9 = 26.1 \text{ ''}$$

Proportionate E. M. F. disappearing as chemical work:

$$4.48 \times \frac{26.0}{74.9} = 1.55 \text{ volts}$$
$$4.47 \times \frac{26.1}{76.0} = 1.54 \text{ ''}$$

The average of six tests made in this manner gave 1.59 volts, as representing the chemical work done, agreeing closely with that required to separate H_2 and O from sulphuric acid, and very poorly with the chemical work as calculated from the heat of formation, viz., 28,150 calories per Eq = 1.23 volts.

When a copper cathode and lead anode were used in $CuSO_4.200H_2O$ electrolyte, the voltage absorbed in chemical work was 1.33 during the first ten minutes, with a back e. m. f., on interrupting the circuit, of 1.32 volts.

Metallurgical Laboratory,
Lehigh University.

DISCUSSION.

MR. REED: Was the loss of heat carried away by the gas as formed taken into consideration? In other words, how did you determine the losses of heat other than that due to the electrochemical action—the loss of heat that would occur when the gases are evolved, by the gases carrying it away?

PROF. RICHARDS: The rise in temperature is only some thousandths of a degree, and the amount of heat that would be carried away by the gases at that temperature is totally negligible. I calculated, also, the amount of water which those gases would evaporate and carry away, saturated, and the heat of vaporization of the water which the gases would take away would not appear in significant figures.

PRESIDENT HERING: There seems to me to be another factor which ought to be considered here—namely, the energy of the expansion of the gases. The gas in this case expands greatly; I think it is about 1,600 times in volume in changing from water to gas, and during that expansion there must be some energy reactions taking place; it seems to me they are important to consider.

PROF. F. B. CROCKER: I would like to ask if Prof. Richards has checked his results by deducting from the total voltage the resistance drop, which ought to give the voltage used for chemical work. There is still another method of checking this voltage, and that is, to open the circuit when the full current is flowing and as quickly as possible to measure the electromotive force. The voltage must be measured rather quickly by an instrument that does not take much current, otherwise there would be a drop. It seems to me that either of these methods would serve as a check upon the results which Prof. Richards obtains calorimetrically.

DR. C. P. STEINMETZ: A method which I believe would give the dissociation voltage of water with high accuracy, is the determination of the potential difference across the electrolytic cell by oscillograph immediately after closing and immediately after opening the circuit, and comparing these two values. In the last years we have used the oscillograph quite extensively for determining instantaneous changes of resistance, etc., for instance, recording the variation of resistance of a silicon rod, when by an excess of impressed voltage it is raised to the melting point in a fraction of a second, and we have found the oscillograph very convenient and suitable for such investigations.

Regarding the voltage equivalent of the expansion of the gases, I do not believe it comes into consideration here. Using the thermochemical equation,

$$2H_2 \text{ gas} + O_2 \text{ gas} = 2H_2O \text{ liquid} + C \text{ calories},$$

then the electrical equivalent of the energy C would give the dissociation voltage of liquid water into hydrogen gas and oxygen gas—that is, the expansion energy is already included in the quantity C of the thermochemical equation.

PRESIDENT HERING: Is it a fact that the expansion energy is a part of the voltage of decomposition?

DR. C. P. STEINMETZ: Yes.

PRESIDENT HERING: Is that certain?

DR. C. P. STEINMETZ: Yes.

MR. REED: I do not believe that is certain. It seems to me that any substance which is deposited by electrochemical action must be an electric conductor, and a gas, therefore, when deposited must be deposited in solution. I do not see any reason why we should assume that oxygen and hydrogen are deposited in that gaseous condition any more than chlorine, and chlorine, as we know, is not deposited in the gaseous state, but in solution. It appears as a solution at first, but when the solution has become supersaturated, of course, the chlorine gas is then given off just the same as any gas would be given off from a supersaturated solution. Oxygen and hydrogen are much less soluble than chlorine, and consequently these gases appear to be evolved almost instantly. But I do not believe there is any proof that any gas is deposited in the gaseous state by the electric current. It seems to me, on the contrary, that the evidence is that those gases are deposited in the liquid state in solution. One striking proof of this is the fact that where the current is exceedingly small, there is no visible evolution of gas.

MR. MOTT: Concerning the instantaneous discharge, I would like to call attention to the fact that it is not always a measure of the chemical energy. Of this, we have a number of instances, such as the aluminum condenser, where the discharge potential may be very high, even 200 and 300 volts, and with lead electrodes in certain electrolytes, there have been obtained discharge voltages as high as 16 volts, and with bismuth as high as 10 volts. These high voltages are several times greater than any possible electrochemical voltage of decomposition. So the instantaneous discharge voltage is not always a measure of the chemical energy.

PROF. RICHARDS: In reply to Prof. Crocker's remark that voltage absorbed in decomposition might be calculated, I have made a number of tests in that way, and because of the unsatisfactory outcome of those tests I have tried to get a method which would be free from those objections. If you make measurements at one voltage and subtract from it the voltage absorbed in overcoming ohmic resistance, the electromotive force of decomposition which you will get will be a certain quantity; if you make measurements with another voltage, you get a different value, and in general that difference increases, being greater the larger the voltage applied and the current passing through the cell. It is because of the unsatisfactory nature of this method of getting the voltage absorbed in decomposition that I tried to get it in another way which I thought would be free from any theories whatever. I agree thoroughly with Mr. Steinmetz as to the expansion of the gases being included—that the voltage I obtain represents the combination of the gases to liquid water, because the thermochemical data are based on the same premises. So if you want to compare it with the thermochemical data, you compare the calculated voltage of the union of the gases to liquid water with the voltage which is absorbed when the gases are liberated from liquid water.

MR. SPERRY: Does the recombination factor there—an impoverishing factor at the surface of the electrode—have any influence on the results?

PROF. RICHARDS: I arranged a thermometer on a stand and provided vigorous stirring through a slit in the cover, and found by that means that sometimes the thermometer would stand to a thousandth of a degree five minutes before the experiment was made; I think the stirring was satisfactory. That was one of the troubles with my first experiments—I found that the stirring was not satisfactory until I arrived at the method of stirring vigorously a certain number of times at a certain period between the readings, and then got satisfactory results.

PRESIDENT HERING: There are reasons to doubt whether the expansion energy really appears in the voltage, or whether it comes over from the heat in the liquid. It would be interesting to know, for instance, what would happen in such a case as this: Assume a strong vessel to be absolutely closed and filled with water, which is then decomposed into gases electrolytically. We know that it would be decomposed at a much lower voltage than in the open air—that is, it would take less energy to decompose the water; you could then get an amount of energy back by letting the gases expand to atmospheric pressure in an engine. In other words, it would take less energy as represented by the voltage, and even were some of this gotten back in the second part of the process, in which the energy must evidently come from the heat of the gases. It leads to a rather interesting problem.

Mr. Patton: One point has been neglected, or perhaps not made sufficiently clear, and that is, that we are assuming that there is a definite decomposition voltage.

Prof. Richards: I have not attempted to get anything except what the figures lead to, and believe that, if you adopt the calorimetrical method, the energy which is lost, and does not appear as heat, represents so much voltage absorbed in chemical change, and where it goes to or what business it does I have not made any assumptions at all about. I simply give you the result, that when you pass a current through that cell, and heat appears as sensible heat, which is measured, an amount of energy disappears which is equivalent to that amount of voltage. Now as to what that voltage does which disappears I have not made any assumptions at all. It is a very interesting theoretical question as to what it does, but do you not see that if you make experiments under different conditions and get different voltages absorbed, you would be simply substantiating the point of view that you have different voltages absorbed under different conditions? I am simply trying to find out what voltages are absorbed under certain conditions when liberating oxygen and hydrogen from dilute sulphuric acid.

Mr. Reed: I fail to see how you can tell what the voltage of decomposition is, unless you know with certainty whether the gases, as held by Dr. Steinmetz, are liberated electrolytically as gases, or whether they are liberated in solution, and the solution, on becoming supersaturated, evolves gases, in which case they would expand and absorb sensible heat from the liquid. If the latter assumption is correct, the heat absorbed by expansion must come from the sensible heat, and not from the electrical energy. If the other theory is true, it must come from the electrical energy. Therefore, until that question can be settled, it seems to me you cannot settle with certainty what the exact voltage of decomposition is.

President Hering: I am afraid this is a question which cannot be settled by a discussion, but only by experiment.

A paper read at the Eleventh General Meeting of the American Electrochemical Society, in Philadelphia, Pa., May 3, 1907; President Carl Hering in the chair.

THE CURRENT EFFICIENCY OF AN ELECTROLYTIC CELL.

By Wm. Roy Mott.

Current efficiency is of wide and practical importance in applied electrochemistry, but it has received only limited theoretical attention in the standard text-books, although the practical conditions are stated with the greatest detail. In this article an elementary treatment is given, dealing more especially with losses. The manufacturer takes most interest in how much money the process yields, regardless of its efficiency, but the applied electrochemist is concerned with wasted material and energy which might be saved.

Three cases are discussed, showing the losses as they originate in current efficiency at different current densities. The anode and cathode processes are treated separately; current efficiency of the cell as a whole is without meaning, since the anode and cathode reactions are independent.

Case I. This is here defined as the case where only one chemical reaction occurs at the electrode, and that reaction follows Faraday's law. For every current density, the efficiency is, of course, 100 per cent. This simple relation does not exist ordinarily, although, for practical purposes, it may be close enough in many plating baths. But diffusion currents and residual currents from other sources interfere in most baths, becoming very pronounced at low current densities. Case I does not exist in the absolute sense for any known process, although within wide ranges of current density it holds very closely, in the deposition of silver, for instance. At very low current density and also at very high current density the departures from 100 per cent. efficiency become decidedly marked.

Case II. The most common case of losses affecting the current efficiency is where the metal or other product is used up at an approximately constant rate by chemical action. Lead, plated out in a fused bath, is redissolved at a certain constant rate. Lithium, plated out in alcoholic solution, is slightly redissolved, giving off hydrogen at a constant rate.[1] Hence, it follows that the current efficiency curves can be expressed in the following simple form:

$$E = \frac{C - A}{C}$$

Where E is the efficiency, *i. e.*, the useful current (C — A) divided by the total current, C, and A is the current wasted because of chemical corrosion of the deposited electrode product. C and A are expressed in amperes per unit area of active electrode surface. Where the efficiency, E, is given in per cent., a factor of 100 is introduced.

The quantity A is of general application. We express rate of corrosion in too many ways—as ounces per square foot per day, grams per square centimeter per hour, etc. So it is here recommended to express all rates of chemical action, taking place at surfaces, in amperes per unit area. In this way uniformity could be secured in expressing rate of chemical action at a surface. This mode of expression is brief and exact, and is consistent with the chemical idea of units, *i. e.*, that of chemical reacting weights.

Consideration of the above formula shows that we have here an electrical method for determining rate of chemical action. The value of A may be obtained from the voltage-current curve, but is given more accurately by an actual efficiency test using the formula. When the polarization suddenly rises, there is a change in the action at the electrode, the rate of chemical action being exceeded by the rate of the electrochemical deposition of products. In a given efficiency determination, the value of A can be readily calculated if the rate of chemical corrosion is fairly constant (Case II). Some further light might be given on rates of chemical action in general by the use of these electrochemical methods. The value A should be considered as a first approximation, applicable to a limited number of cases. The more refined consideration of A as a variable will not be taken up here.

In Table I is given the calculated efficiency for different

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[1] See Patten and Mott, Decomposition Curves of Lithium Chloride in Alcohols, and the Electrodeposition of Lithium, Jour. Phys. Chem., *8*, 152-195 (1904).

current densities, where A is assumed to be equal in value to one ampere per square foot. These figures are representative of conditions that may exist in electrode deposition from a slightly acidified solution. The data are plotted on Plate I, together with a typical current = e. m. f. diagram showing the correspondence of the value of A with the rise in voltage at the electrode.

TABLE I.

Data for an Efficiency Curve with a Single Constant Corrosion Loss of One Ampere per Square Foot.

Current Density in Amperes per Square Foot	Efficiency Per Cent.	Loss Per Cent.	Current Density in Amperes per Square Foot	Efficiency Per Cent.	Loss Per Cent.
1	0.	100.0	10	90.0	10.0
2	50.0	50.0	20	95.0	5.0
3	66.7	33.3	30	96.7	3.3
4	75.0	25.0	40	97.5	2.5
5	80.0	20.0	50	90.0	2.0
6	83.3	16.7	100	98.0	1.0
7	85.7	14.3	1000	99.9	0.1
8	87.8	12.2	10000	99.99	0.01
9	88.9	11.1			

Fig. 1 contains a typical voltage-current curve (I), the ordinates being volts and the abscissas amperes per square foot. The current density interval marked A represents the current wasted in depositing material, which is immediately removed from the electrode (or corroded) by the chemical action of the plating bath. The sudden rise in the curve at 1.0 ampere per square foot is due to the appearance upon the electrode of the main product of the electrolytic process, and from this point on the cell begins to work efficiently. The rise in efficiency as the current density increases is given by Curve II, its abscissas being the same as for Curve I, but its ordinates, E, the per cent. efficiency, calculated from Curve I by the use of the formula $E = \frac{C - A}{C}$, and noted at the left of the plate, while the per cent. loss (due to chemical corrosion of the main product) is given in reverse order on the right-hand ordinate and is indicated by the same curve (II), since the loss is the inverse of the efficiency.

The variation of A as conditions other than the current density change, deserves some attention. Of course, this is a plain case of study of rate of chemical action as the concentrations, temperature, and other factors vary.

First, suppose the loss A is due to the reaction of the solvent on the electrode product. If the electrode product is above molecular thickness, then the concentrations of both reacting parts are fixed, although the reaction product may not be fixed in concentration, but this we will temporarily ignore. Under these hypothetical conditions, the temperature is the only variable left. This acts in logarithmic ratio. Table II gives an example of how the temperature affects A, and therefore affects the efficiency, which is calculated for two current densities (see Plate 2). This is to illustrate what would be expected of efficiencies as the temperature is changed. In Table II, it is assumed that A decreases by one-half in value every time the temperature is lowered by 15° C.; or A is doubled in value every time the temperature is raised 15° C. This is the characteristic way in

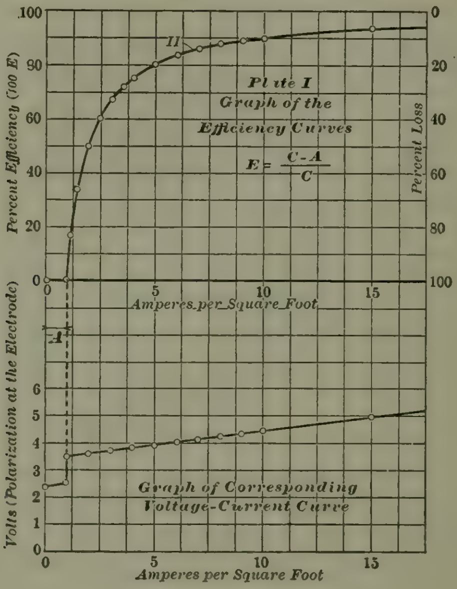

FIG. 1.

which rate of chemical action changes with temperature, although usually a smaller temperature interval is required than in the assumed case.

TABLE II.

*Effect of Temperature on the Constant A.**

Temperature Centigrade	Value of A Amperes / sq. ft.	Efficiency at 5 Amperes / sq. ft.	Efficiency at 10 Amperes / sq. ft.
—5	.125	97.5	98.75
+10	.25	95.0	97.5
25	.5	90.0	95.0
40	1.0	80.0	90.0
55	2.0	60.0	80.0
70	4.0	20.0	60.0
85	8.0	0.0	20.0
100	16.0	0.0	0.0
90	10.0	0.0	0.0

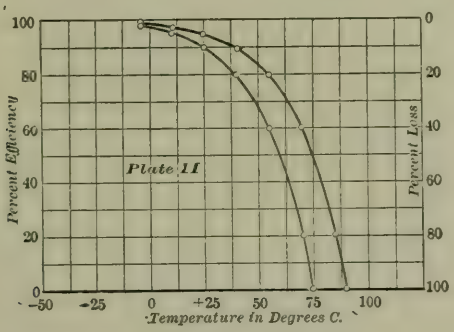

FIG. 2.

The curves in Fig. 2 show the decrease in efficiency as the temperature rises. Ordinates are per cent. efficiency at the left and per cent. loss at the right; abscissas are degrees Centigrade. Curve I is for a current density of 5 amperes per square foot, and Curve II for 10 amperes per square foot, the wasted current due to chemical corrosion of electrode product (A) being taken as 1.0 ampere per square foot at 40° C.

It is beyond the scope of this article to discuss the exponential

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* A remains constant only in the given equation, and in the plane of that equation. As soon as another variable factor, such as temperature, appears in the equation it becomes tri-dimensional, and A varies in the *temperature-corrosion* plane, but still is constant in the *corrosion-total current density* plane.

function of A and T which might be inserted in the efficiency equation, but the logarithmic formula expressing this relation may be useful:

$$\text{Log } A = \log A_T + \frac{T_2 - T_1}{R} \cdot \log 2$$

A_T equals the constant loss at T; $(T_2 - T_1)$ is the total rise in temperature, and R, the constant rise in temperature required to just double A.

Second, if the loss A be considered as depending not on the chemical action of the solvent upon the electrode product, but on the corrosive effect of the material in solution, then the concentration enters as a factor. The loss, A, is largely proportional to the concentration of the dissolved oxidized agents at the cathode, or of reducing agents at the anode. The effect of temperature on A approaches a linear function, as does that of the temperature coefficient for rate of diffusion. If the rate of diffusion exceeds the inherent rate of the chemical reaction, then the temperature affects A in a logarithmic ratio; but if the rate of chemical reaction inherently exceeds the rate of diffusion, then the rate of chemical action is merely an expression of rate ot diffusion, and in the latter instance the loss A is nearly proportional to the temperature, increasing as the temperature increases. If the loss A depends most on the rate of diffusion, then all stirring of the solution greatly increases A. The failure to deposit zinc from a solution of zinc salt impinging on a cathode, when deposition would readily occur with the same current density from a quiet solution, is a good illustration of this.

Case II is very simple and, of course, has only a limited application. It might be called the case of two reactions, although it may be extended to an electrolysis involving a number of reactions. Most electrochemical processes involve at least two sets of electrochemical or chemical reactions at each electrode. Even in refined work on electrochemical equivalents there is some variation that should be ascribed to A.

The third case is intended to illustrate how three chemical processes at the electrode affect current efficiency where the product of the intermediate process is useful.

Case III. As the current rises, the efficiency considerations of Case II hold until the third reaction takes place. Let this point in the current density be called B. Then the efficiency for the intermediate product is represented by the formula,

$$E = \frac{B - A}{C}$$

The efficiency now passes through an acute maximum. In order to compare the form of the curve with actual efficiency curves, the calculated curve has been plotted, where B is assumed equal to five amperes per square foot.

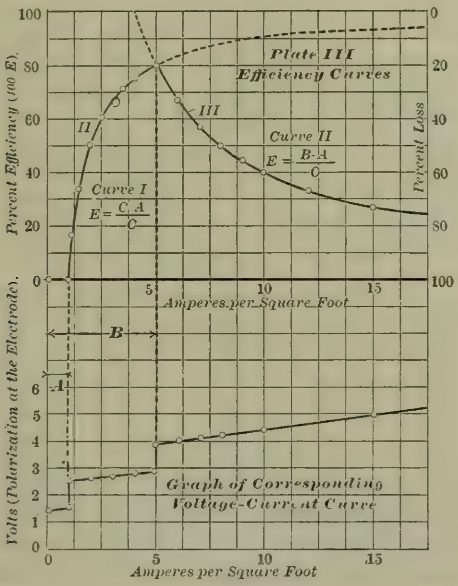

FIG. 3.

The determination of B from the current-e. m f. diagram is made in the same way as for A. The calculated data for the efficiency where a third reaction takes place is given in Table III. The curves in Fig. 3 are drawn from this data, the upper and lower halves of the plate corresponding to those in Fig. 1. Ordinates of the lower Curve I are volts (polarization at the electrode), and abscissas current density expressed as amperes per square foot. The space A represents the loss due to chemical corrosion of the first product of electrolysis, whose appearance upon the electrode is characterized by the first steep rise in the curve; the space B shows the loss due to the corrosion, A, plus the current used in forming the first product. In the upper half of Fig. 3, Curve II gives the increase of efficiency in forming the increasing current density, the dotted portion indicating the path, provided the second reaction had not set in. Curve III shows the greater and greater decrease in efficiency in forming the intermediate product, as more and more current, at higher current density, is used to form the new third product, which begins to form at B current density.

TABLE III.

*Hypothetical Data for the Efficiency Curve of an Intermediate Product.**

Current Density in Amperes per sq. ft.	**Loss A**	**Loss B**	**Efficiency Per Cent.**
1	1	0	0.0
2	1	0	50.0
3	1	0	66.7
4	1	0	75.0
5	1	0	80.0
6	1	1	66.7
7	1	2	57·0
8	1	3	50.0
9	1	4	45·0
10	1	5	40.0

Curve II and its extension, III, are familiar, except for the sharp maximum, which does not appear in experimental work, since the current density at the electrode varies more or less at different points on the electrode surface. This smooths out the experimental curve at the sharp maximum, and at the point of zero efficiency, *i. e.*, at current density A. This effect is very slight if the potential rise is large at A and at B. Also the

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* The following concrete example will make clear the use of the term ***intermediate product:*** In the electrolysis of lithium dissolved in amyl alcohol, we may wish to consider hydrogen as the useful intermediate product. At very low current density no hydrogen appears at the cathode, since it is oxidized by substances dissolved in the solution; but as the natural density increases the hydrogen is liberated with greater and greater efficiency until metallic lithium is deposited. Thus we are justified in terming hydrogen an intermediate product, in that it is liberated in the current-density interval which lies above the region of residual current, and below the point at which metallic lithium first appears. After the metal is once deposited the hydrogen is formed with less and less efficiency as the current density increases, since relatively more of the current goes into the separation of the metal.

efficiency Curves, II and III, with average uniform current densities, and the curve for an average of current density that changes over the surface or with the time, exactly coincide at a little distance from the sharp maximum. The mathematical proof of this is not given here.

The interrelations of A and B under different conditions might well have been discussed completely, but it is sufficient to say that those conditions which influence A are, in their theoretical aspect, applicable to B. The electrolytic production of iodoform and the electrolytic deposition of chromium are probably examples of Case III.

Case IV. This is where two substances are produced at the electrode simultaneously in a fixed ratio. Probably such cases exist, but we have too little data for exact treatment.

In conclusion, the quantities A and B should be considered not as absolute constants, but as variables which may even be influenced by the current density. However, they are fixed, not by the current itself, but, as with any true chemical reaction, by the mass law, by the temperature, by the rates of diffusion toward and away from the surface of the electrode, etc.

As the energy efficiency equals the voltage efficiency times the current efficiency, the energy efficiency curve may be plotted on the same plate with the current efficiency curve and the voltage-e. m. f. diagram. To illustrate this, if, with the data on Fig. 1, we calculate the three efficiencies at 15 amperes per square foot, we have as follows: Current efficiency, 93 per cent.; voltage efficiency, 68 per cent.; energy efficiency, 63 per cent.; at 10 amperes per square foot the values become: Current efficiency, 90 per cent.; voltage efficiency, 74 per cent., and energy efficiency, 67 per cent. From a practical standpoint, the higher energy efficiency may not be the best if the current efficiency is lower, for two reasons—first, the increased size of plant necessary, and second, the greater quantity of waste products to take care of.

Summary. Some of the ordinary forms of current efficiency curves are given a theoretical interpretation which is intended to be more suggestive than conclusive. These interpretations are more or less well known, and no novelty is claimed for them, unless it be the plea that all reactions at surfaces should be expressed in terms of current density; this is the thing to do, if all chemical action is merely electrochemical action at molecular distances. This leads to clearness of thought and simplicity of expression.

Attention is called to an electrochemical method of measuring rates of chemical reaction by observations on the voltage-current curves. The same rate of chemical reaction can be calculated by the well-known formula for current efficiency, from current efficiency curves.

DISCUSSION.

Prof. J. W. Richards: I think that Mr. Mott has made a useful suggestion when he pleads for expressing the rate of chemical corrosion which takes place during an electrolytic process in terms of the current density. That represents the amount of waste of electrical energy or electrical quantity which occurs by reason of the chemical action occurring in the cell. I think the suggestion is a good one, and will be very useful to the workers in the electrolytic field.

The other point which he has brought out, is that which concerns the efficiency output of an electrolytic process. We look at the ampere output as being one of the most important factors in the electrolytic process, and yet the total energy efficiency is really, in many cases, the financial criterion of the process. So that, other things being equal, it is not always the process whose ampere efficiency is the highest which is the cheapest, but the process whose energy efficiency is the highest. I think, by calling attention to this difference, Mr. Mott has also done a useful service.

Mr. Carl Hering (communicated): Mr. Mott's suggestion to represent the purely chemical actions at the electrodes in terms of current density seems ingenious, as it enables this quantity to be introduced into a formula in the same terms as the electrolytic reactions, thus greatly simplifying the formula. It remains to be shown, however, whether that quantity is sufficiently constant, or varies in a sufficiently regular way to be of more than very limited application. There are many varying conditions which will alter the amount of chemical reaction at the electrodes. In the electrolysis of zinc sulphate, for instance, with an insoluble anode, the apparent loss of zinc on the cathode will depend very greatly on the amount of free acid, which is continually increasing; at first, much zinc will be deposited, while later it will be almost impossible to get any at all. Not only does the free acid redissolve the deposited zinc, but more and more of the current will decompose the acid instead of the zinc sulphate (the former being more easily decomposed). Hence, his quantity A will vary greatly. As to temperature, it seems to me to be very unsafe to assume that there is any fixed law, except, perhaps, in special cases and over very limited ranges. Some chemical reactions will not take place at all below certain temperatures, while above that they suddenly take place very vigorously, like in the case of the combination of carbon and oxygen.

W. D. BANCROFT (communicated): I think that Mr. Mott's paper is full of inaccuracies. I question his statement that current efficiency has received only limited theoretical attention in the standard text-books. I question his statement that "current efficiency of the cell as a whole is without meaning, since the anode and the cathode reactions are independent." One might as well say that there was no meaning in speaking of the cost of an article to a retailer, because the cost of manufacturing and the cost of distribution (freight, etc.) are independent. We certainly have to consider current efficiency for the cell as a whole in the manufacture of hypochlorite and of chlorate.

It is legitimate to express corrosion in grams per square centimeter or in equivalent weights per square centimeter, but Mr. Mott's unit of amperes per square centimeter means absolutely nothing, unless we postulate some definite current efficiency, presumably 100 per cent. How is one to express the electrolytic corrosion of a nickel anode in a sulphate solution in terms of amperes per square centimeter? Even if one could do it, it would be unsatisfactory, because one often wishes to study the amount of corrosion with varying current density.

Mr. Mott has considered two cases—one in which there is no loss, and one in which there is a constant loss per unit of time. Mr. Mott says that the amount of the constant loss can be determined from the voltage-current curve, but he does not explain how this can be done, and, personally, I question the statement. Mr. Mott himself admits that it is easier to determine the value from a direct measurement of current efficiency.

Mr. Mott assumes that the chemical rate of attack will double in value every time the temperature is raised 15° C., because "this is the characteristic way in which rate of chemical action changes with temperature, although usually a smaller temperature interval is required than in the assumed case." It looks as though Mr. Mott were reasoning from reactions in homogeneous systems to reactions in heterogeneous systems.

It does not seem to me that a paper like this helps the Society. As a member of the Committee on Papers, I protested against the reading of this paper at Philadelphia. As a member of the Committee on Publication, I protested against the inclusion of this paper in the Transactions.

Mr. Mott (communicated): Mr. Hering has pointed out that in the continued electrolysis of zinc sulphate, there will be an increasing amount of free acid so that the value of the quantity A will necessarily be altered. This is absolutely correct and must follow if the quantity A depends on the factors that control ordinary chemical reaction. In order that the quantity A be constant, we must have fixed concentrations of the reacting part, a fixed temperature and a fixed rate of circulation of the electrolytic solution.

As regards the temperature effect, there are many limitations to the assumption of a fixed law, as Mr. Hering and Dr. Bancroft hold. As stated in the paper, the temperature effect lies between two limiting conditions—the curve of the effect will not exceed the logarthmic law and will not be less than the linear law rate of change of diffusion with the temperature. With small concentrations of the reacting chemical, the linear law of the effect of temperature holds best; but where the concentration of the reacting chemical is very great then the logarithmic law best applies. The inherent complexity of the effect leaves much to be done experimentally. In the electrolysis of fused salts, the loss can be largely conditioned on the rate of diffusion by using enclosed electrodes. It is under these conditions that the loss varies with the temperature closely in a linear manner.

The following data show precisely the point that it is desired to make clear. These data are derived from the results given by Lorenz in his paper on electrolysis of fused salts, read before the American Electrochemical Society in 1904.

Temperature.	Enclosed Electrode	Unenclosed Electrode.
600 C.	0.7%	12%
700 C.	1.5%	25%
800 C.	2.2%	50%
900 C.	3.9% (?)	100% (?)

These are the per cent. losses in the electrolysis of fused zinc chloride and correspond to the quantity A. With the enclosed electrode, the loss increases in a linear manner as the temperature increases. With the unenclosed electrode, the loss increases in a logarithmic manner with the temperature. Of course there must be continuity of connection of the two formulæ, as the degree of enclosure is varied. From either formula, we predict, first, that electric furnaces depending on electrolysis should be very carefully controled as regards their temperature, and second, that many unstable and now unknown substances will be formed by electrolysis at very low temperature—say that of liquid air.

Dr. Bancroft questions my statement that "current efficiency of the cell as a whole is without meaning since the anode and cathode reactions are independent." Mr. O. W. Brown[1] obtained, with a nickel-plating bath, an anode current efficiency of 46.29 per cent. with a smooth ground cast nickel anode and a cathode current efficiency of 75.42 per cent. I don't see that the average of these efficiencies or their sum could have any significance or meaning. The analogy that Dr. Bancroft proposes is quite incorrect since it refers to a single article, but should refer to a single article decomposed into several articles. I should like to know if Dr. Bancroft can give a current efficiency of the above nickel-plating bath as a whole. In the manufacture of chlorate, we have two independent efficiencies to be considered. The total production of chlorate is the chlorate made at the anode less that lost at the cathode. If we wish to express the total result as the current efficiency of the cell as a whole, there is no objection for this special case from a practical standpoint, but from a scientific standpoint there is considerable objection because of the inexactness and incompleteness of the expression. Suppose we said the

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[1] Trans. Am. Electrochem. Soc., *4*, p. 87, 1903.

current efficiency of the cell as a whole was 60 per cent. This might mean that the anode current efficiency was 60 per cent., and that no chlorate was reduced at the cathode. Again, it might mean that the anode current efficiency was 80 per cent., but that the reduction at the cathode used up chlorate corresponding to 20 per cent., thus leaving an apparent efficiency of 60 per cent. The bare statement therefore of 60 per cent. current efficiency might mean several different things as regards the actual electrode efficiencies. It seems self-evident that the two electrode processes should be separately considered.

Dr. Bancroft has misunderstood the suggestion of the use of amperes per square centimeter as the unit of rate corrosion. The mistake is made in comparing "grams per square centimeter or equivalents per square centimeter" to current density. We should compare grams per square centimeter *per unit time* to current density. Dr. Bancroft has stated no legitimate unit of rate of corrosion. The following units of rate of corrosion might legitimately be added:

Grams per square centimeter per second.
Grams per square centimeter per day.
Grams per square centimeter per year.

Equivalent weight in grams per square centimeter per second. In fact, we might multiply a reasonable choice of units very greatly. Depth of metal in inches corroded per year is a useful unit for the designers of metal structures. Volume of gas per unit area per unit time given off by metal in acid bath has been used in various forms. Of course, the standard basis of most of the units of rate of chemical corrosion have been expressed in weight units removed per unit area per unit time. Almost every conceivable mixture of the units of the metric system and of the English system have been used with each of the time units—second, minute, hour, day, week, month and year. It was precisely this varied and unscientific assortment of units that should be eliminated by using the equivalent current density in amperes per square centimeter for expressing the rate of chemical corrosion.

By equivalent current density, we mean the current density that would be required to deposit or remove by Faraday's law the same quantity of metal per unit area per unit time as was removed by chemical corrosion. The equivalent current density may have a real physical significance and would correspond to the magnitude of the sum of the total local currents divided by the total area. Local action is now very generally used in the theory of the chemical corrosion of metals. Very pure zinc is scarcely corroded at all, but a small percentage of iron may increase the rate of corrosion by 50 times. This current might be called the local current of corrosion.

Without going into the details of a further reply, I give below in symbols here used the general formula that Lorenz and Appleberg have worked out.

$$\text{Efficiency} = \frac{C^N - A}{C^N}$$

In a particular experiment the value of N was found to be 0.83 instead of 1.00 used in the formula below.

$$\text{Efficiency} = \frac{C - A}{C}$$

Both these formulæ are of the nature of approximations which need to be improved. I wish to point out finally that the chemical corrosion may be of the same sign as the electrolytic, which correctly allows of an interpretation of the interesting results of apparent efficiencies of over 100 per cent. In fact, where there is a zinc anode in sulphuric acid, the apparent current efficiency may assume enormous values, but the form of the curve is approximately described by the same formula with the required change in the sign of the quantity A.

$$\text{Apparent current efficiency} = \frac{C + A}{C}$$

A formula of this type describes the anode corrosion by an electric current in a bath in which there is corrosion when no external current is applied. Of course, the formation of an insoluble film at high current densities alters the case with the nickel anode referred to by Dr. Bancroft.

A paper read by title at the Eleventh General Meeting of the American Electrochemical Society, in Philadelphia, Pa., May 4, 1907; President Carl Hering in the chair.

ON THE DENSITY, ELECTRICAL CONDUCTIVITY, AND VISCOSITY OF FUSED SALTS.

By H. M. GOODWIN and R. D. MAILEY.

The present paper contains a résumé of the results obtained in an extended research on certain properties of fused electrolytes which was carried out during 1905 and 1906 in the Research Laboratory of Physical Chemistry at the Mass. Inst. of Technology. The experimental details of the research and numerical results will be published shortly in the *Physical Review*. For a complete résumé of the literature on this subject, see Part II of Prof. Lorenz's admirable work, "Electrolyse Geschmolzener Salze."

The object of the investigation was to determine with as high a degree of precision as possible the effect of temperature upon the molecular conductance and fluidity of a series of fused salts, when pure and when mixed with one another, in order to throw some light upon the effect of temperature upon their degree of ionization, and also upon the relationship announced by Foussereau, in 1886, between the conductivity and viscosity of fused electrolytes.

For this purpose, three distinct investigations were necessary: First, the measurement of the density of the salts over a wide range of temperature; second, the measurement of their conductance, and third, the measurement of their viscosity over a corresponding temperature interval.

The salts chosen were sodium nitrate, potassium nitrate, lithium nitrate, silver nitrate, and silver chlorate, salts melting between about 250° and 350°, and forming mixtures with each other in all proportions. The precision aimed at in the density measurements was 0.1 per cent. or better, and in the conductivity and viscosity measurements, 0.5 per cent. This precision, however, was not attained in the viscosity determinations, owing to experimental difficulties encountered. These results are probably reliable to not more than one percent. A precision of the order of magnitude desired in our work necessitated the measurement of the actual temperatures (not merely temperature differences) to a few tenths of a degree, as the temperature coefficient of conductivity of the salts investigated was, in some cases, as high as 0.7 per cent. per degree. This was accomplished by measuring the temperatures thermoelectrically, balancing the thermoelectric force of a Pt-Rh couple against a known fraction of a standard cadmium cell. The deflection of a low resistance d'Arsonval galvanometer served as indicating instrument. One millimeter deflection (at a distance of 2.5 meters) corresponded to a variation of 0.8° C., hence, by estimation, temperatures could be measured to 0.1°. The junction was calibrated at the following fixed points: Boiling water, naphthalene, benzophenone, and sulphur, the respective temperatures, at 760 mm. pressure, being taken as 100.00°, 217.68°, 305.44°, and 444.52°. A large calibration plot, 100 x 100 cm. served for interpolating temperatures corresponding to any measured thermoelectric force.

Three electric furnaces were employed for maintaining constant temperatures; the one used in the density measurements was of the vertical platinum resistance type, and another consisted of a large bath of fused nitrate, the temperature of which was regulated by electric heating. The temperature could be rapidly lowered, when required, by means of a spiral steel cooling coil, through which a slow stream of water was allowed to flow, the open end being connected with the sink. The viscosity apparatus was immersed directly in this bath; the conductivity apparatus, on the other hand, was suspended in a small air chamber of cast iron which was lowered into a bath of molten lead and tin. For details of construction, reference must be made to the complete article.

Density Measurements:

The density determinations were made by a modified Westphal balance, in which the sinker was constructed of fused quartz, the coefficient of expansion of which was known. In the case of the heavier silver salts, a platinum ball suspended from the pan of a delicate analytical balance was used. These sinkers were immersed in the molten salt, which was fused in a large platinum crucible placed in the furnace beneath the table upon which the balance was set. These methods are both capable of high precision and are not difficult to carry out.

Conductivity Measurements:

After experimenting with methods previously used for determining the conductivity of fused salts, which in general have led to widely discordant results, we finally devised a cell which up to about 500° C. has given excellent results when used in connection with the well-known Kohlrausch alternating current (telephone) method. Such a cell should be constructed of a substance which up to the maximum temperature at which it is to be used, is first, a non-conductor; second, chemically inert with respect to the salts which it is to contain; third, capable of being formed into a cell, the constant of which is invariable or may be calculated with varying temperature, and fourth, of such a form that the actual resistance of the contained fused salt shall be not less than about 100 ohms, while the electrode surface is large, in order that a good minimum may be obtained in the telephone.

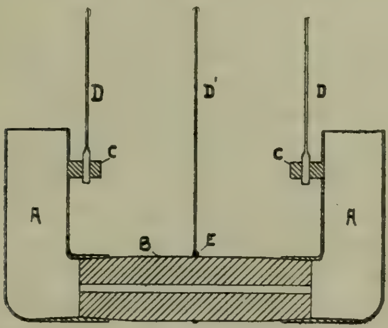

FIG. 1.

A substance admirably fulfilling these conditions is quartz, either in the vitreous or natural crystalline form. The design of cell which we devised is shown in Fig. 1, which is drawn to scale. B is a cylinder of rock crystal cut parallel to its axis, through which a capillary, 1.5 mm. in diameter is bored, with a diamond drill. The ends are ground to a slight taper. The ends of this cylinder are closed by platinum elbows, A, carefully ground to fit, which, in turn, form the two electrodes of the cell. They are so designed that the flow lines from the end of the capillary spread out over a large platinum surface, thus reducing the effect of polarization to a minimum. The cell is suspended in the furnace by means of platinum leads, DD, attached to the elbows by means of platinum plugs inserted in small platinum blocks, CC.

It was originally intended to use fused quartz for this cylinder, in order to eliminate the effect of temperature on the cell constant, but, owing to the large differential expansion between this substance and platinum, the cell invariably began to leak when the temperature was raised to 300° or 400° C. We therefore chose natural quartz crystal instead, as the coefficient of expansion of a crystal at right angles to its axis happens fortunately to be very nearly that of platinum. The effect of the very slight leakage which was sometimes observed was corrected for by measuring, by means of an auxiliary platinum wire electrode, D′E, wound around the middle of the cylinder, the leakage current along the outside of the cylinder. The correction for change of cell constant with the temperature could be accurately calculated, as the expansion coefficients of quartz along both its axes are well known. With this cell the conductivity of fused salts can be measured with a tone minimum as perfect as that obtained under the best conditions with aqueous solutions at ordinary temperatures. The cell constant was determined by a normal sulphuric acid solution at 18° C.

Viscosity Measurements:

These were decidedly more difficult to obtain with a high degree of precision than conductivity measurements. The only measurements on record at the time we began our work were a few isolated determinations by Foussereau, published in 1886, on sodium and potassium nitrate, in which Pouisseuille's capillary method was used.

Very recently, however, this same method has been applied by Kalmus[1] to a repetition and extension of Foussereau's experi-

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[1] Inaugural Dissertation, Zürich, 1906. To be published shortly.

ments, with results which will be considered later. Dr. Kalmus has also been good enough to assist in checking up a number of our viscosity determinations, for which and for other assistance in the preparation of this research for publication we desire here to express our appreciation and thanks.

Preliminary measurements with capillaries made from the various samples of the hard glass at our disposal showed an etching effect of the nitrate on the glass capillary, and caused us to abandon this material. Fused silica capillaries would have been admirably adapted to our purpose, but these could not be obtained of the necessary dimensions in this country. We decided, therefore, to use a platinum capillary, and devised a viscosity apparatus, the form of which is shown in Fig. 2. This is essentially a modification of the well-known form of apparatus recommended by Ostwald for measuring relative viscosity, but made entirely of metal, preferably of platinum. In our apparatus, the reservoir was made of silver, to reduce expense; the remainder was of platinum. The capillary, C, was 0.6 mm. diameter and 10 cm. long, and enclosed in an outer tube of platinum, 3 mm. in diameter, to protect it from injury. The salt was first introduced as powder, and then melted in the reservoir,

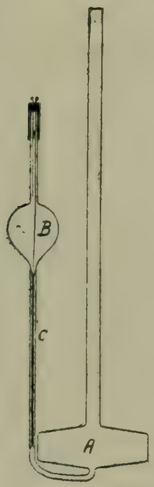

FIG. 2.

A (about 100 cc. capacity). It was then forced up, by means of compressed air, through the capillary C until the bulb B was completely filled, and then allowed to flow back into A under the influence of gravity. The novel feature of the apparatus was the method of noting the time it took the liqiud in the bulb B to flow back through the capillary.

This was accomplished by noting the time the surface of the liquid broke contact first, with a very fine platinum electrode extending nearly down to the top of the bulb B, and second, with a similar independent electrode adjusted to the lower end of the bulb, where it joined the capillary. The time of breaking these circuits was noted by a telephone placed in series with an induction coil. When the two electrodes were properly centered, the time of flow could be determined with a precision of about one second in 800 seconds. The whole apparatus was immersed in the fused nitrate bath, thus enabling a very uniform temperature to be maintained throughout. This form of apparatus has the advantage that if constructed wholly of platinum, it may be used for viscosity measurements up to the decomposition point of almost any liquid. The apparatus gives relative results, and has therefore to be calibrated by means of a liquid of accurately known viscosity. For this purpose the constants of the apparatus were determined with water at two different temperatures.[2] It was then tested on a one per cent solution of sodium chloride, the viscosity of which was known and approximately equal to that of the fused nitrates. The agreement obtained was excellent, within 0.1 to 0.3 per cent. It should be stated, however, that the constants of our apparatus varied in an irregular and unexplained manner from time to time in much the same way as described by Bousfield[3] in his researches. We therefore made it a point to determine its constants with water immediately before and after every series of measurements. If the constants were found to have changed by over 0.75 per cent., the measurement was discarded. The agreement was usually much better than this, in which case the mean value of the constants before and after the run was taken in the computation.

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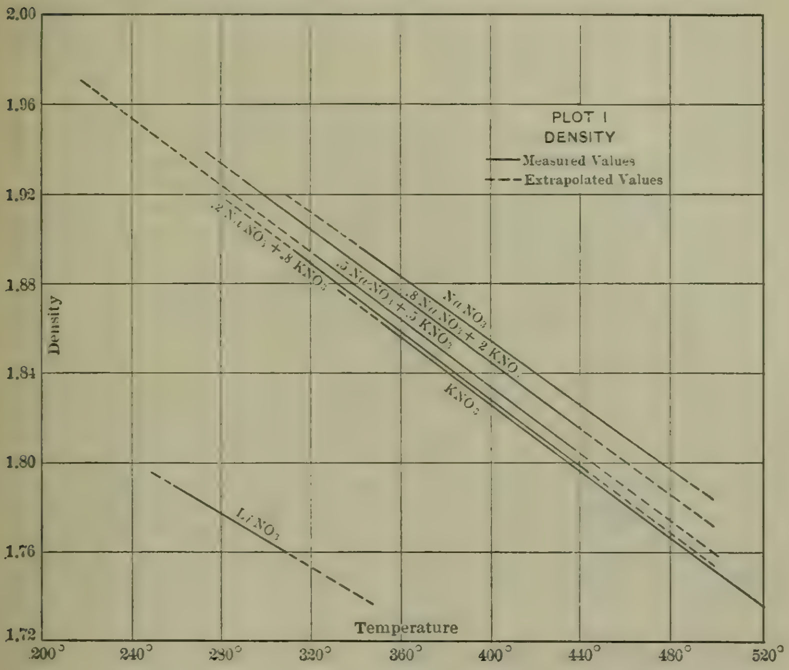
[2] For discussion of corrections applied see unabridged article.

[3] W. R. Bousfield, Zeit. fur Phys. Chem., *53*, 257, 1905.

Summary of Results.

The final results of our investigation may be summarized as follows:

1. The curves representing the change of density with the temperature of sodium, potassium, lithium, and silver nitrate and silver chlorate, together with mixtures of sodium and potassium nitrate and of lithium nitrate and silver chlorate are shown in Plots I, II, and III.



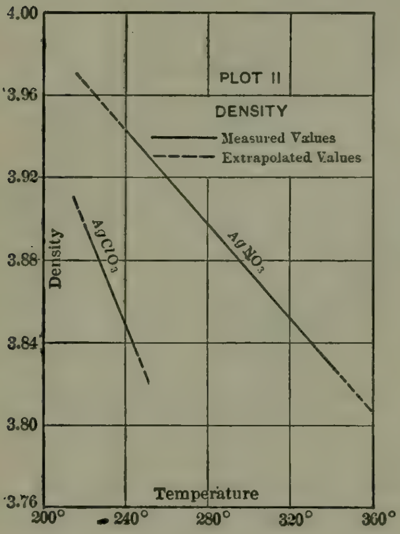
In all cases, the density is a linear function of the temperature over the range of temperature investigated, to within a tenth of a per cent. From these curves, tables giving the *specific* and *molecular* volume for every ten degrees have been computed.

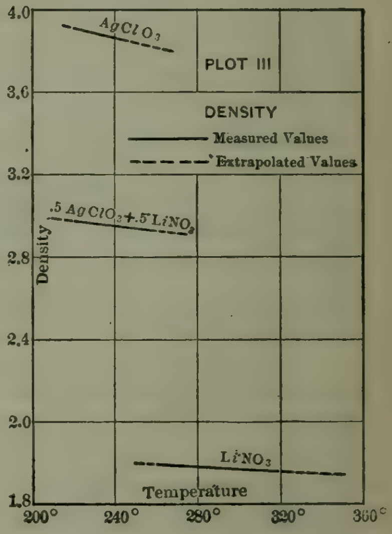
2. The specific volume of mixtures of sodium and potassium nitrate, containing 8 and 2, 5 and 5, and 2 and 8 mols of these salts respectively, is greater than that computed from the specific volumes of the components, *i. e.*, the solution of one salt in another

is accompanied by an expansion. The magnitude of this expansion is small, being a maximum, 0.5 per cent., for the equimolecular mixture.

In the case of an equimolecular mixture of lithium nitrate and silver chlorate, on the other hand, a contraction of about 20 per cent. occurs. (See Plot III.)

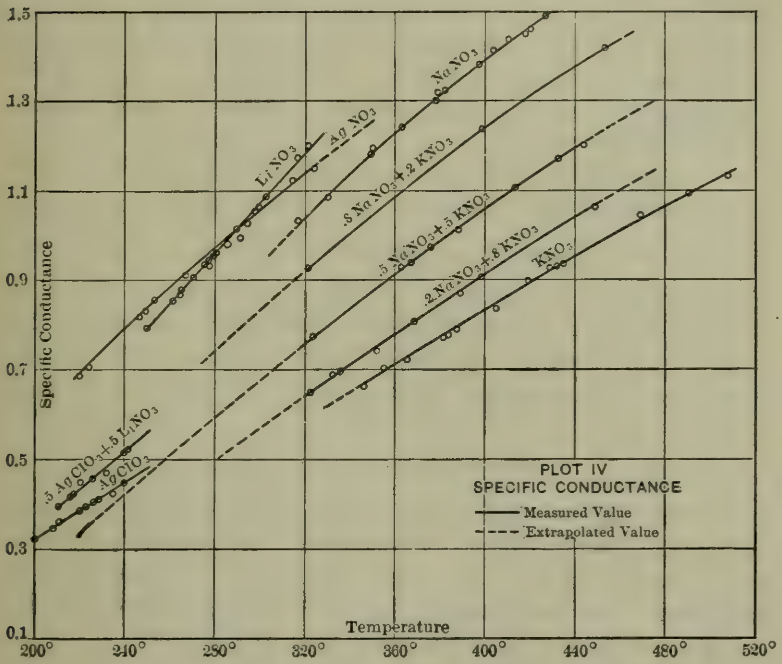
3. The results on the variation of the specific conductance with the temperature are shown in Plot IV. The dotted portions of the curves indicate an extrapolation of the data to the observed melting points of the salts. It is seen that, except in the case of lithium nitrate and silver chlorate, which could be measured over only a limited range of temperature on account of their instability, the specific conductance is not strictly proportional to the temperature, but increases less and less rapidly as the temperature rises. For the limited range of temperatures over which lithium nitrate, silver chlorate, and their mixture was studied, the specific conductance is proportional to the temperature. From these curves, the specific and equivalent conductance has been calculated for every ten degrees, as well as the temperature coefficient for each interval. The temperature





coefficient is, generally speaking, less than one-fifth that for aqueous solutions.

4. A study of the computed values of the equivalent conductance shows that this quantity increases very nearly linearly with the temperature. The temperature coefficient decreases, therefore, with increasing temperature, but at any given temperature is slightly greater than that of the specific conductance at the same temperature.



5. The equivalent conductance of the mixtures of the sodium and potassium nitrate is *less* than that computed from the equivalent conductance of the components. This is most marked in the case of the equimolecular mixture, where the difference reaches 3 per cent., an amount considerably greater than can be accounted for by experimental error. It tends to confirm the view advanced by one of us that the effect of dissolving one nitrate in another is to decrease the dissociation. Our results

do not confirm the conclusion drawn by Poincaré from similar experiments on the conductivity of mixed nitrates. He concluded that the conductance of a mixture could be calculated from that of the components, but as his results showed deviations of several per cent., the relation brought out by our data could not have been evident from Poincaré's results.

6. In the case of an equimolecular mixture of lithium nitrate and silver chlorate, the deviations between observed and computed values of the equivalent conductance are much greater (as much as 12 per cent.), the computed values being greater as before, indicating a metathesis between the components, with corresponding change (decrease) of ionization. It will be remembered, also, that this mixture showed a very marked contraction in volume.

7. Instead of considering the viscosity coefficient η of the salts and its variation with temperature and relation to conductivity, we have investigated its reciprocal, $F = \frac{1}{\eta}$, *i. e.,* the fluidity. The variation of this quantity with the temperature is shown in Plot V. In all cases, the fluidity is directly proportional to the temperature. Its temperature coefficient is in every case greater than the corresponding temperature coefficient of specific conductance.

8. The ratio $\frac{\text{specific conductance}}{\text{fluidity}} = \frac{K}{F}$, has been computed for every ten degrees, and found to decrease regularly, without exception, with increasing temperature. Foussereau's law of the proportionality between these quantities is therefore not confirmed. Our results are, however, in excellent agreement, so far as comparison is possible, with those of Kalmus.[4]

9. We have also computed the value of

$$f = \frac{\text{fluidity}}{\text{molecular volume}} = \frac{F}{\varphi}$$

which quantity we have called molal fluidity, and its temperature coefficient for each ten degrees. The results show that the molal fluidity is directly proportional to the temperature. The ratio of $\frac{\text{equivalent conductance}}{\text{molal fluidity}} = \frac{\lambda}{f}$ has also been calculated for every ten degrees.

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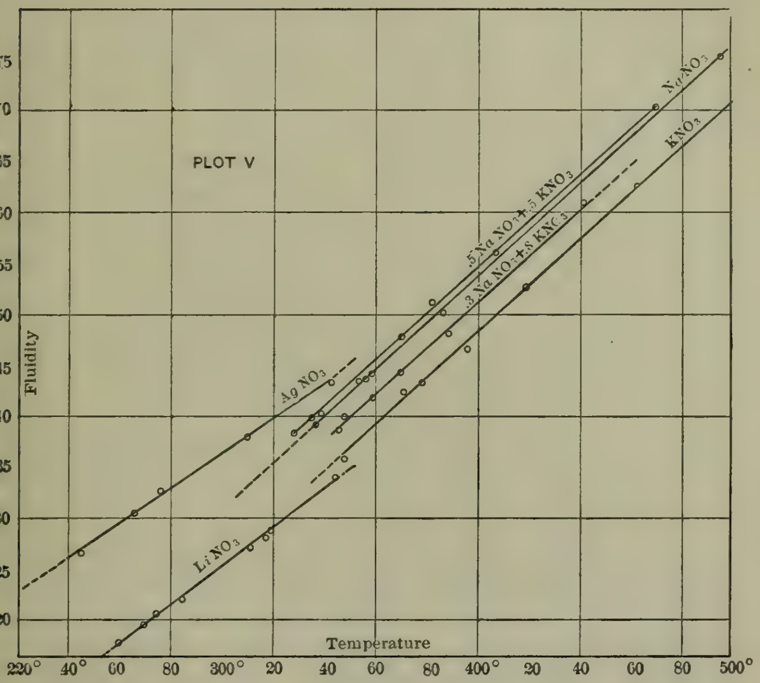
[4] Dissertation, Zürich, 1906.

This ratio is practically a constant for potassium nitrate and for mixtures of potassium and sodium nitrate over a range of temperature of more than 100°. In the case of sodium, lithium and silver nitrates, the proportionality does not appear to hold quite as rigidly; the ratio decreases with increasing temperature. Thus, the ratio for sodium nitrate decreases from 56 at 350° to 54 at 450°; for silver nitrate, from 56.3 at 250° to 54.3 at 350°; for lithium nitrate, from 71.8 at 250° to 65.0 at 300°.



If we assume that conduction in fused salts takes place in a similar manner to conduction in solutions, then

$$\lambda_t = \gamma_t (u + v)_t$$

where γ is the ionization constant of the salt and u and v are the ionic conductances. Both γ and $(u + v)$ are functions of the temperature. If we assume that the ionic velocities are proportional to the fluidity of the medium through which the ions move, *i. e.*, $f^t = k(u + v)_t$ where k = constant, then

$$\frac{\lambda}{f_t} = \frac{\gamma_t}{k} = k^1 \gamma_t$$

Hence, comparing the ratio of $\left(\frac{\lambda}{f}\right)$ at two different temperatures will give a measure of the change of dissociation of the salt between these temperatures. From such a comparison it appears that increasing the temperature tends to diminish the dissociation of fused salts investigated. The decrease in dissociation is very small or zero in the case of potassium nitrate and its mixtures with sodium nitrate; for silver nitrate, it is 4.2 per cent. per 100°; for sodium nitrate, 6.4 per cent. per 100°; for lithium nitrate, 11 per cent. for 60°.

This result is not astonishing; the recent accurate determinations of Noyes on the ionization of salts at high temperatures in aqueous solution show that here also increasing the temperature produces a very marked diminution in the dissociation of the dissolved salt. Furthermore, the enormous increase in the conductivity of a salt at its melting point as it passes from the solid to the liquid state (an isothermal phenomenon) clearly points to some other factor than temperature as the cause to which its increase in value is to be chiefly ascribed.

If the assumptions upon which the above conclusion is based are true, we may further conclude that the above nitrates ionize in the fused state with evolution of heat.

10. The molal fluidity of a mixture of sodium and potassium nitrate is greater than that computed from the fluidity of the components of the mixture. The difference is nearly constant for a given mixture, *i. e.*, independent of the temperature; it is greatest for equimolecular mixtures. As the equivalent conductance of these same mixtures was found to be less than the calculated values, we have additional evidence that the effect of increased fluidity on the migration velocity of the ions is probably opposed by a diminished dissociation of the mixed salts.

11. The preceding results provide a more reliable experimental basis for the development of a theory of conduction in fused salts than has hitherto been possible. Although the accumulation

of these data is laborious, since it involves three independent investigations on density, conductivity, and viscosity, all of which are of more than ordinary difficulty if a precision of 1 per cent. or better is desired, it is to be hoped that other contributions to this interesting and important field will be made in the near future.

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A paper read at the Eleventh General Meeting of the American Electrochemical Society, in Philadelphia, Pa., May 4, 1907; President Carl Hering in the chair.

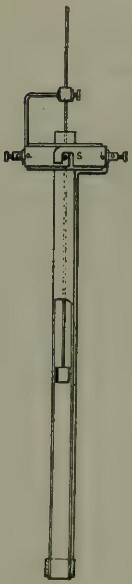
RAPID MEASUREMENT OF ELECTROLYTIC RESISTANCE.

By Charles F. Burgess.

The specific resistance of an electrolyte varies in a marked degree with variations in concentration, temperature, and purity. Notwitstanding this fact, comparatively little use of resistance seems to be made in the handling of solutions in technical operations. An increase in the amount of various acids and salts in aqueous solutions from 5 parts to 10 parts per hundred produces a decrease of approximately 50 per cent. in the specific resistance, while the corresponding variation in the specific gravity is in the neighborhood of 3 per cent. The sensitiveness, therefore, of a resistance measurement as a means of determining the strength of a solution is materially greater than that of a density determination. The degree with which water approaches purity may be more readily judged by a resistance measurement than by a measurement of its specific gravity.

In technical works, where solutions are handled, the control is usually effected by the use of the hydrometer and by chemical analysis. Devices for the determination of specific resistance are scarcely known outside of the laboratory, though the sensitiveness and range of its measurements are greater than those obtained by the hydrometer. Resistance measurements, correctly interpreted, may, in many cases, enable chemical analyses to be dispensed with, Even in electrochemical work, where the specific resistance has a practical significance, other than in throwing light upon the composition of solution, little use is made of this measurement. The electro-plater makes daily use of his hydrometer, but knows the "resistometer," if it may be so called, only as a laboratory instrument.

The lack of a more extensive practical use of specific resistance measurements may perhaps be found in the fact that the methods of measurement are not sufficiently simple and accurate. While the hydrometer measurement requires only the immersion of a graduated glass tube into the electrolyte, the measurement of resistance usually requires that a sample of the solution be transferred to a calibrated glass vessel and measurements made with instruments of a cost which may be objectionable. Unless troublesome precautions are taken, the temperature of the electrolyte in the testing cell may differ from that of the main body of the electrolyte, and temperature corrections must therefore be made.



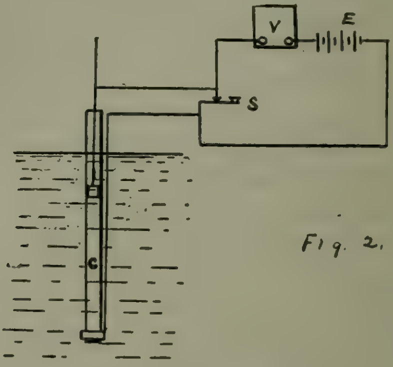


Fig. 2.

A description is here given of a simple method of resistance measurement, which has been in successful use in the Applied Electrochemistry laboratories of the University of Wisconsin for several years, and by which the time and trouble required for taking a reading is little greater than that needed for determining the temperature by means of a thermometer, or the specific gravity by a hydrometer. Aside from features of simplicity and convenience, the method has been found to give results sufficiently accurate for many technical purposes, and the possibility also exists, where suitable precautions are taken, of attaining a considerable degree of precision, as required in research work.

No new principles are involved in this method, which is based upon the fact that a resistance placed in series with a voltmeter and a source of electrical pressure decreases the voltmeter reading. The apparatus required consists of a glass tube with suitable electrodes, as shown in Fig. 1, a voltmeter of the ordinary type, and a source of constant electrical pressure, such as may be cheaply and conveniently furnished by a few dry cells connected in series. The electrode tube, as illustrated in Fig. 1, consists of a glass tube, with its upper end passing through a square ebonite block. Upon this block are mounted the two binding posts, one of which makes connection to an adjustable electrode placed inside of the tube, and the other to a fixed electrode placed outside of the tube near the bottom. The two terminals are kept normally short-circuited by means of the spring,*s,* and this contact may be broken by pressure of the fingers applied at the points *a* and *b*. The operation of the measurement consists in connecting the tube terminals through a voltmeter to a source of constant pressure, as shown diagrammatically in Fig. 2. The tube is dipped into the electrolyte so that both electrodes are immersed. The electrodes being normally short-circuited by the switch, *s,* the column of electrolyte, *c,* is placed in series with the voltmeter and, consequently, decreases the voltmeter reading. The resistance of the column of electrolyte, *c,* is represented by the expression.

$$R = R' \frac{E - E'}{E'}$$

Where R′ is the resistance of the voltmeter, E is the total pressure measured with the switch closed, and E′ is the reading of the voltmeter with the switch open. The specific resistance may be derived from this value by knowing the dimensions of the column of electrolyte or by calibrating the instrument with a standard solution.

With the electrodes fixed at a certain distance apart, and with an unvarying source of pressure, a voltmeter may be calibrated so as to indicate directly the specific resistance.

There is an advantage in the fact that the column of electrolyte is at the same temperature as the main body of the liquid; and the instantaneous flow of current, which is necessary in taking the voltmeter reading, cannot heat the electrolyte to an amount sufficient to cause appreciable variation of temperature.

This method is simply a modification of the fall of potential method of resistance determination, in which the voltmeter is made to serve the purpose of both voltmeter and amperemeter. It is necessary that the resistance of the voltmeter be accurately known, and this instrument should preferably be of the high resistance type. The voltmeter made by the American Electrical Instrument Company, having a resistance of exactly 100 ohms per volt of scale division is especially convenient for this purpose.

It is evident that for the highest degree of sensitiveness, the dimensions of the column of electrolyte should be adjusted so as to be somewhere near equal to the resistance of the voltmeter. For a tube from 0.5 to 1 centimeter in diameter and about 20 centimeters long, a voltmeter reading from 6 to 10 volts should be suitable when measuring electrolytes of high conductivity. A higher voltage may be used to advantage when high resistance solutions are being studied.

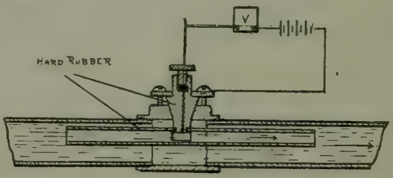


Fig. 3.

A source of error, which must be recognized, is the polarization which may exist between the two electrodes when connected in series with the voltmeter. This may be eliminated by taking readings with the inner electrode set successively in two different positions, but in practice it is preferable to choose the electrodes of such materials that the polarization may be negligible. For example, in measurement of copper solutions, copper electrodes should be employed. It is evident that the higher the voltage employed the less is the percentage of error possible by polarization, and this constitutes an advantage in the use of higher pressures.

Various modifications of this method naturally suggest themselves. The tube, instead of being straight, may be bent in such form as may be most convenient.

Where a record is desired on a solution flowing through a pipe, it may be obtained in the manner illustrated in Fig 3, where a hard rubber tube within the metal pipe carrying the liquid has a branch which projects through the walls of the pipe, and which carries the wire leading to the electrode. The pipe thus serves as one of the electrodes, the columns of electrolyte, on both sides of the inner electrode being in parallel. An example of the application of this device is its use in the discharge pipe of a filter press, the voltmeter indicating the completeness of the washing of a filter cake.

It is evident that this method of measurement lends itself readily to the use of a recording voltmeter.

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DISCUSSION.

MR. J. L. WILLS: I would like to ask Prof. Burgess if the polarization is negligible, or if it enters into consideration?

PROF. C. F. BURGESS: The polarization has to be taken care of. Platinum electrodes in sulphuric acid solution will give a polarization of over a volt. With 6 volts applied pressure, this polarization may introduce an error of 15 per cent. The instrument, with electrodes at fixed distance, may be calibrated so as to take that into account, or electrodes may be chosen to reduce polarization to a minimum; for example, if using a copper sulphate solution, copper electrodes would be used. Another method of reducing or eliminating polarization errors is to employ a high pressure, say 100 volts, which is possible when using a glass tube of small bore. The polarization would then come down to a pretty small percentage of error. This is intended as a convenient technical instrument, rather than a highly accurate scientific one.

PRESIDENT HERING: I think Prof. Burgess should have emphasized the fact more strongly that the polarization must be recognized; if the polarization be neglected, it may in some cases lead to very large errors. I calculated two cases as illustrations; in one of them the resistances were selected as is recommended; the error was 35 per cent.; another, in which a resistance of the solution was one-tenth that of the voltmeter, and the error was 194 per cent.; that is nearly three times the true resistance, which shows that the method is not applicable at all if the polarization is neglected, unless it is eliminated. In other words, the counter e. m. f., when reduced to its equivalent as resistance, may become a very large quantity. Prof. Burgess says that the electrodes should always be chosen so that the polarization may be neglected. This often cannot be done; hence, the second method he suggests may very often have to be used, and I would suggest that it might be well if he would add the formula for that second method, in which two measurements are made to determine the resistance.

In reading over the paper, another method suggests itself to me which eliminates some of the difficulties. It is simply a substitution method, using the same tube that he describes, but connecting it in series with an adjustable known resistance and a voltmeter. A plug resistance is preferable. Plug this resistance to zero, set the electrode up to the highest point in the tube, and take the reading of the voltmeter. Then move the electrode down a certain known distance, and adjust the resistance until the voltmeter reads the same. Then the reading of this resistance is the resistance of that column of liquid. You merely substitute a known resistance for the unknown one, and in that way the polarization is absolutely eliminated, because it occurs in both measurements; the polarization is, moreover, the same in both, because the current is the same; the current is the same because the voltmeter reads the same. In the second method which is described, he also makes two readings, so that my method involves no more work than his second method. Furthermore, you do not have to know the resistance of the voltmeter. The polarization is not eliminated approximately, but absolutely. In Prof. Burgess' second method it is only approximately eliminated, because the currents in the two different readings are different. Moreover, you do not have to know the resistance of your voltmeter, and it does not have to read correctly in volts; a mere indicator or galvanometer would answer, and there are no calculations involved; the reading is direct.

Prof. C. F. Burgess: I would say that the purpose of this arrangement is to simplify the method just described. Mr.

Hering proposes using a voltmeter and a calibrated resistance, and says that it isn't necessary to know the resistance of the voltmeter, but a voltmeter always has fixed resistance; and why not make use of it if possible? By using the voltmeter resistance we can do away with the calibrated resistance. The polarization error can be almost completely eliminated by moving the internal electrode, the tube being graduated as a burette, first having the inner electrode at a certain position, and taking the voltmeter reading, and then moving it a given distance while observing the change in voltmeter reading. It is a very simple calculation to see how much resistance it takes to produce the observed change of voltmeter reading.

President Hering: This is what I referred to as the second method you described. Of course, if it is an objection to have a second calibrated resistance, the method you describe is better than the one I mention.

Mr. Grower: Temperature has a big effect on specific resistance. The errors from temperature in ordinary hydrometer measurements are never more than a few per cent., whereas the specific resistance will vary 20 or 30 per cent., due to ordinary variations of temperature. Where the temperature is approximately known, I think the method is pretty good.

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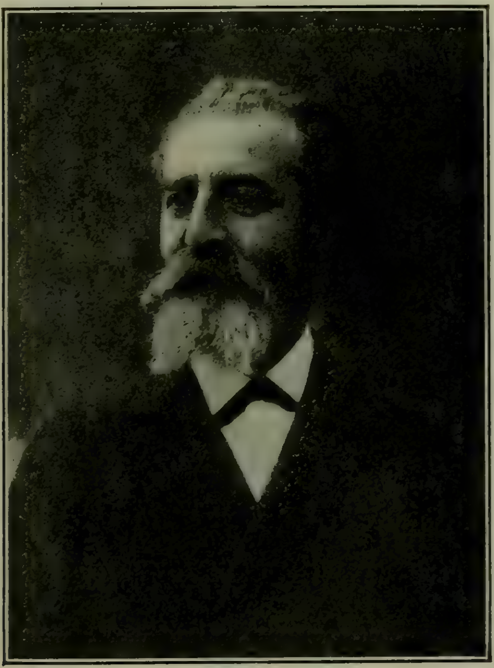
HENRI MOISSAN.

By George Frederick Kunz.

The untimely death of Henri Moissan has removed from the world one of the most brilliant and distinguished scientific investigators of our time. Whether regarded as a student of pure science, or as a discoverer and promoter of important practical applications, no man has exceeded him, and very few have even approached him, in the lifetime of the present generation. His



Henri Moissan

departure at the early age of fifty-five, in the very fulness of his powers, is an irreparable loss to science everywhere and peculiarly to science in France. It seems remarkable in this respect that the only other men who had attained to any similar prominence in the same domain of chemistry and physics, Dr. Pierre Curie and more recently the great Berthelot should have likewise died in the midst of their activity, within less than a year past. The whole scientific world can but join in sympathy with France, both in her grief at the loss of Moissan, and in the pride that she justly feels in one who shed such glory upon his country, whose name will be recognized in all coming time as ranking among those who have made great and permanent discoveries in the realm of chemistry and physics, and have also given to mankind practical applications of the highest importance.

It is difficult, within the limits of a brief obituary, to give adequate expression to the variety, the novelty, and the importance of the researches and discoveries of Dr. Moissan. He had found and developed fields of research that were peculiarly his own; and in those fields he vastly enlarged the scope of human knowledge, while incidentally he gave to the world results of immense economic and industrial value. The whole department of electro-chemistry, with its apparently unlimited applications, had in him its pioneer explorer and its triumphant expounder. His whole magnificent scientific career was achieved within the brief limit of about twenty-five years, and we cannot but wonder what further triumphs he might have won, had his life been spared to the ordinary bounds, and lament with deepest sorrow the sudden termination of a course so fruitful already in results and still so full of promise and possibility.

Prof. Moissan was born September 28, 1852, in the city of Paris, where his whole life was spent and his whole work achieved. His scientific education was chiefly in the Musée de l' Histoire Naturelle of that city. Here, in 1872, at the age of twenty, he entered the laboratory of Frémy, and followed up his chemical studies under such masters as Deville, Debray, Berthelot and St. Claire Deville. "His early training," says Prof. R. S. Hutton, in an obituary notice of Moissan, "firmly fixed the direction of his life's work, for it is precisely along the lines so ably developed by this brilliant school of French chemists, that

Moissan's genius and resource in experimentation were applied. Worthily to have upheld the traditions and high quality of this school required powers of no mean order."[1]

In the very next year, 1873, he became an assistant in the laboratory of Decaisne and Dehérain, in the same great Academie. Here his studies were directed toward vegetable chemistry, and his first formal contribution to science, published in 1874, was a joint study with M. Dehérain upon the action of plants in the dark, in absorbing oxygen and giving out carbon dioxide. But the bent of his mind was more toward inorganic chemistry, and he ere long withdrew from this association and established a laboratory of his own, where he began some of his most important investigations. He subsequently entered into connection with the laboratory of Debray and Troost, where he continued his researches until, in 1879, he was appointed instructor and demonstrator in the laboratory of the École superieure de Pharmacie. In 1887, after his great success in isolating fluorine, he was made professor of toxicology in the same institution, and later was transferred to the chair of mineralogical chemistry.

All these earlier years were full of scientific activity. In 1877 he began investigations upon the salts of chromium, which, in the words of Becquerel, "signalized him as an able experimenter." These, extended into a series of valuable papers upon the oxides of iron, manganese, nickel and chromium, were presented in 1880 as his thesis for the degree of Doctor in Science. He had already begun his investigations in regard to the electric furnace, and was also engaged in the effort to achieve the isolation of fluorine. Prof. Becquerel, speaking on the death of Moissan before the French Academy of Sciences, depicts vividly this remarkable quest, carried on through years, for the "unattainable body which had eluded his predecessors and his masters." He conducted the siege systematically, and each unsuccessful endeavor brought him nearer to his object, until the day when, in an electrolysis of hydrofluoric acid, which was accidentally impure, a gas appeared at the positive pole—and this was fluorine! A powerful current was employed, at a low temperature (—23° C.), and the impurity which determined the fortunate success was a small amount of potassium bi-fluoride, which had been added to

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[1] Nature, Feb. 28, 1907, pp. 419, 420.

the anhydrous acid. He had previously made many skilful efforts to separate fluorine from its combinations with silicon, boron and arsenic; but now at last he had reached a result which Prof. Hutton calls "one of the greatest achievements of chemistry in the nineteenth century." The first notice of the experiment was made to the Academy of Sciences on June 28, 1886, and fuller details were presented a few weeks later. On November 8th, Prof. Debray announced to the Academy the complete acceptance of Moissan's results by the section of chemistry.

The demonstration was now given, for the first time, of the reality and the properties of this previously theoretical element, and of the exact composition of hydrofluoric acid, and its precise correspondence to the other halogen acids. These results and experiments led him to further studies of fluorine compounds and to the discovery and preparation of a number of new ones. From these he naturally passed to the study of other binary compounds, especially those of boron, silicon and carbon, in which he afterwards attained results that were scarcely less important and novel.

This great triumph in the isolation of fluorine at once made Moissan famous in the world of chemistry, and won for him the Lacaze prize from the French Academy, and the professorship of toxicology in the École de Pharmacie. Twenty years later, in the last year of his life, a medal was given him by students and friends in commemoration of this early achievement, and he received also the great Nobel prize, which was largely due to this discovery, though it also recognized his later work in many forms.

As Prof. Moissan's interest inclined chiefly toward the study of the elements and their inorganic compounds, toxicology was evidently not to be his best field of activity. So in 1889 he was transferred to the chair of mineralogical chemistry in the École de Pharmacie. Here he remained for a number of years, and carried out much of his finest and most conspicuous work. In 1897 he lectured upon fluorine at the Royal Institution in London, and on the following day, in conjunction with Sir James Dewar, he accomplished the liquefaction of fluorine in the laboratory of that institution. His extended researches upon this notable element and its combinations were published in 1900, in a volume entitled "Le Fluor et ses Composés."

In the same year he was appointed professor of general chemistry in the Sorbonne, and speedily became Director of the Institute of Applied Chemistry.

It is largely, however, to his remarkable work upon carbon and the carbides, and his triumphs with the electric furnace, that Prof. Moissan's fame is due with the general public. Very interesting it is to trace the connection between these and his earlier studies. His peculiar interest in the elements and their problems has already been mentioned, and after his great success with fluorine, and indeed before, his mind was powerfully drawn toward the mystery of the diamond and its origin—the problem of the crystallization of carbon. With this object in view, he sought to reach some results from combinations of carbon with fluorine, and succeeded in producing two gaseous compounds of those elements, but their decomposition set free the carbon only in the amorphous form. He was thus led to extended studies upon the three modifications of carbon, the conditions of their formation, and their possible production from one another. This investigation was in itself of great value in adding largely to the knowledge of these varieties of carbon and their relations and metamorphoses. Gradually he came to recognize the fact that the crystallization of carbon as diamond, the hard and heavy form, instead of graphite, the soft and less dense variety, must be dependent upon great pressure. He was now on the road that led him to the actual production of diamonds.

The problem before him thus became that of causing carbon to solidify under great compression. The only way seemed to lie in the direction of the solubility of carbon in fused metals, and for this very high temperatures were necessary. He had long been much interested in the electric furnace and its possibilities, and conducted a host of experiments with it and obtained important results. Among these were especially the carbides of many metals, formed at the enormous temperatures attainable by the electric furnace. The solubility of carbon in molten iron had long been known, but whenever it separated out in cooling it took the form of graphite. If the solidification could be made under extreme pressure, he reasoned, diamond carbon should be obtained. Here was the key to the long-sought mystery. Availing himself of the well-known property of iron, of expanding in solidification (like water), he melted iron in a crucible in the electric furnace, at a temperature of 4000°, introduced pure carbon in the form of sugar charcoal, and when it was freely dissolved, removed the crucible and quickly immersed it in cold water. The exterior of the mass of course solidified at once, leaving the interior portion confined and unable to expand, so that it was forced to solidify under enormous pressure. The result followed as he had expected, part of the carbon being found to have crystallized in the form of minute diamonds.

This was the great success, achieved in 1893, which interested the whole world and made the name of Moissan familiar to multitudes who had known little of his previous scientific researches. He had produced real diamonds by an artificial process. They were minute, indeed, and could only be obtained by dissolving the enclosing mass of iron with powerful acids, but they were true diamond crystals. The value of the experiment was theoretical only, for the cost of producing them was very great, and their size too small for any practical use. But the discovery was one of extreme interest in itself, and was a remarkable example of a scientific study carried on through years, with great skill and indomitable perseverance, to the attainment of a desired end.

Three years later, in 1896, Prof. Moissan visited the United States, and repeated these experiments in several brilliant lectures. One of these was given in New York, before a joint meeting of the American Chemical Society, the Academy of Sciences, the American Institute of Electrical Engineers, and the College of Pharmacy. It was a remarkable occasion in every way. Dr. Charles A. Doremus thus describes one of the principal incidents: "As he removed the glowing crucible from within the furnace and plunged it into a mass of water, some of his audience, all scientists, involuntarily moved, as if expecting an explosion. 'Have no fear,' said he, 'I have performed this experiment without accident, over 300 times.' " Of course, it was possible on such an occasion to show the process only, not the results, as the mass of iron must have time to cool completely, and then must be slowly dissolved in the strongest acids, before any diamonds present could be found and tested, but it was very striking to witness the calm confidence of Prof. Moissan in the success which he had so often proved. Laying his hand upon the non-conducting cover of the crucible, he referred again to his oft-repeated experiments, and remarked, "I *know* that this regulus contains diamonds, for I have never had a failure." To one who looked on that commanding figure and noble countenance, it seemed that Moissan might well have been made the subject of a picture, representing "The Triumphant Chemist," as a counterpart to the one known as "The Doubtful Alchemist." The two would illustrate impressively the contrast between modern science, with its clearness and precision, and the indefinite groping of the early period of chemistry.

The studies and experiments that preceded this remarkable achievement had taken a very wide range and led him into some peculiar fields. His researches on the three varieties of carbon have already been mentioned, but in addition to these he had laboriously investigated all the occurrences and associations of diamonds in nature, and, in particular, the presence of carbon in meteorites. The discovery of diamond carbon in the great iron meteorite of Cañon Diablo, which was made by Foote and Koenig in this country in 1891, and verified by Moissan himself and by others abroad, is thought to have had special influence in giving him the conception of the combined agency of great heat and great pressure in the production of diamonds. His examination of the ash of diamonds, and also of the minerals associated with the diamonds of South Africa, impressed him further with the frequent presence of iron in connection with them, and led him on in the line of his endeavors. Nor did the researches cease when he had achieved success; he kept them up year after year, and one of his latest important papers, in 1904, was the record of an elaborate reëxamination of the Cañon Diablo iron and its carbon and diamond inclusions.

But apart from these special researches, Moissan's general fame will always be connected with the electric furnace. His experiments with this wonderful appliance, though largely incidental to his diamond quest, led to many other results, among which are those that have proved most important in their practical bearing, apart from their scientific interest. His production of a whole body of new compounds, formed at temperatures never before attained, marks an epoch in the history of chemical science. These are chiefly silicides, borides, and carbides of various metals, among which two have become especially prominent—the calcium and the silicon carbides. It is true that neither of these was strictly a new discovery by Moissan. Calcium carbide had been well known before, and its property of yielding acetylene gas upon contact with water, but it had been too expensive to be available for that purpose on any considerable scale. In 1892, however, Moissan proved that it could be easily and cheaply produced in the electric furnace, and thus made possible the important industry of acetylene lighting. In the year previous, he had noticed the accidental formation of a compound of carbon and silicon in some of his early experiments with the furnace, but he did not publish it or give it special attention until two years later (1893). By that time the same substance had been independently discovered in this country by Cowles and Acheson, and the latter had described it and given it the name of carborundum. Moissan has freely accorded to Acheson the credit of priority, but he has given much attention to the substance and its important properties, in later publications, especially in his great volume on the electric furnace and its products.[2] This body, known as both silicon carbide and carbon silicide, is now manufactured on a large scale, and has great value as an abrasive, being harder than any substance previously known, except diamond itself. Eleven years afterward, in 1904, during his reëxamination of the Cañon Diablo meteorite, Moissan discovered this identical substance in very small crystals, associated with the diamond carbon present in that iron. Being now found for the first time as a natural product, it became entitled to a scientific name, as a true mineral, and the writer took pleasure in proposing for it the name of Moissanite, in honor of his eminent friend, the discoverer.[3]

But beside these two, Prof. Moissan was the actual discoverer and producer of a number of metallic carbides before entirely unknown, some of which possess remarkable properties. After his visit to the United States in 1896, in recognition of many honors and courtesies extended to him here, he presented to the National Museum, at Washington, a full set of these new and most interesting products, sixteen in number, each with his signa-

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[2] Le Four Electrique, Paris, G. Steinheil, 1897, pp. 385, 8vo.

[3] Am. Jour. Science, vol. XIX, May, 1905.

ture. These were secured largely through the friendly influence of the late Prof. R. Ogden Doremus, of New York, and are a permanent treasure of great interest.

In the following year Moissan published his most important work, Le Four Electrique, in which the instrument of his researches and all its products and applications were treated of systematically and fully.[4] This was the great record of his life-work. "Here," Prof. Hutton says, "his preëminent position is due, not to the design or discovery of a special form of furnace, but rather to the skill with which he investigated in detail a number of individual chemical reactions," and also to the extreme care and accuracy with which all his work was conducted.

Since the opening of the new century Moissan had been gaining honors rapidly, while ever actively engaged in continuing and extending his researches. He had been the recipient of honors from scientific bodies in almost every land. In 1900 he was president of the International Congress of Chemists, held at Paris. In 1904, as already stated, he revisited America, and addressed the scientific convention at St. Louis by invitation of the Government. In 1906, he was awarded the great Nobel prize, his highest honor, and alas! his last.

The economic and industrial results of Prof. Moissan's studies and discoveries have been of the highest practical importance. His friend and co-laborer, Prof. Becquerel, in a most beautiful obituary address before the Académie des Sciences, dwells with great emphasis upon these aspects of his work. Moissan himself, while ever deeply interested in the practical side of his researches, and anxious to establish and enlarge the industries of his country, was not ambitious for rewards or distinctions as an economic scientist, and let this be known as his feeling. All his achievements were inspired by pure love for science, and he gave his results freely to the world, unrestricted by patents or personal limitations, for the use and the profit of others. In this respect, his character and spirit are a noble example of the highest type of scientific devotion. His great success was due to a remarkable combination of faculties—daring conception, fertile imagination, skilful manipulation and extreme accuracy in work, together with indefatigable patience and lofty aim. Prof. Becquerel closes his

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[4] Le Four Electrique; Paris, G. Steinheil, 1897; pp. 385, 8vo.

obituary by quoting a beautiful and noble expression which he had employed: "We should always place our ideal so high that we never can attain it." Such a combination of qualities enabled him to conceive and plan his work, to persevere in the face of countless obstacles, and to bring it to a triumphant issue, in fields that had never before been explored and that had seemed almost hopeless of attainment.

We can but lament that so brilliant a career has been cut short in the very midst of its achievements, after accomplishing so much in a brief quarter-century since the name of Henri Moissan first came into prominence. He died from an operation for appendicitis, in the fulness of his powers and his fame, but his work is immortal in the history of science, and his methods and his character should alike be an inspiration to those who survived and who succeed him.

Of late years, Prof. Moissan had undertaken, with the aid of a group of co-workers and assistants, the preparation of a general treatise upon mineralogical chemistry. Had he lived, this would have been the grand summing-up of all his studies and conclusions, past and prospective, and the fact that it has been interrupted is an irreparable loss to science. At the conference of chemists, held at St. Louis in connection with the Exposition of 1904, Prof. Moissan delivered an address by invitation of the United States Government, which has since been published in Paris, and which was essentially the opening chapter of this great work.[5] It is impossible to read this noble address without feeling that it is the product of a master mind. It begins with a broad and very clear outline of the growth of chemistry from the earliest times to its present position, by the successive labors and investigations of many men in many lands, and shows admirably the progress of thought and the widening of scope in the history of the science. His own experiments and results are next described, in their logical connections with each other and with the problems of chemistry during his lifetime; and then follows the extension of his thought and his forecast into the field of mineralogical chemistry proper, closing with a brief but very broad outlook as to the relations of chemistry with other fields of scientific investigation, especially in physiology and astronomy.

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[5] La Chimie Minérale; ses relations avec les autres sciences; Paris, 1904; pp. 31, roy. oct.

Dr. Moissan's presentation of the development of his own remarkable body of researches and discoveries, as a chapter in the history of chemistry, is of great interest, and may well be briefly reviewed. After tracing the progress of the science, step by step, and its extension into various kindred fields, up to the latter part of the nineteenth century, he proceeds to the subject of thermochemistry—the relations of reactions to temperatures either very high or very low. The great importance of this subject had long been recognized, but the possibilities of experiment were limited. The highest temperatures attainable were those produced by the oxy-hydrogen blowpipe, first used in 1802 by Dr. Hare, of Philadelphia, and later followed up by Deville and Debray in France. But the limit of temperature thus obtained was 1800°—just high enough to admit freely the fusion of platinum, which takes place at 1775°—and was among the first notable results achieved by Hare.

In his desire to produce the crystallization of carbon in the form of diamond, the problem which had such special attraction for Moissan, he undertook minute and comprehensive studies of all the forms in which carbon is known to occur, and of the whole question of its solubility in fused metals. He began his experiments on this latter point with the oxy-hydrogen blowpipe, but found that not only were higher temperatures necessary, but also more exactness and uniformity of conditions. His results were uncertain and variable.

Attempts had repeatedly been made to utilize for both scientific and industrial purposes the much higher temperature of the electric arc, discovered by Davy about the same time with Hare's invention of the oxy-hydrogen blowpipe. But little practical success had attended these attempts, until the comparatively recent invention of the dynamo-electric machine, which opened a new era in the development of chemistry, by the transformation of the current into a source of continuous heat before unattainable.

Prof. Moissan omits any description of his own special type of furnace, passing at once to a general statement of the results which he obtained. The furnace itself is extremely simple, but many questions arose in its application, requiring new study and leading to new results. The temperature of the arc increases with the intensity of the current, and the limit attained, or attainable, has never been exactly determined. In this respect, Moissan says, he was less fortunate than Dewar, who was able to fix definitely the lowest temperature reached, that of the solidification of hydrogen, at —252.5°, only 20.5° above the "absolute zero" of theoretical physics. All the conditions of the current—amperage, voltage, etc.—together with the size of the electrodes, the duration of the experiment, and every circumstance involved, had to be most carefully noted as factors. The volatilization of carbon, as determined by Violle, at 3500°, gives one definite point of temperature, up to and above which Moissan's experiments ranged widely.

His general summary of results is essentially as follows: Most of them are well known, but certain aspects are presented in a very striking manner. He found it possible to decompose readily many metallic oxides before considered irreducible, to dissociate a great number of other compounds, and to produce a whole series of entirely new combinations. In particular, he thus prepared the numerous body of carbides, borides and silicides, that will forever remain associated with his name. Many of these same bodies, moreover, though stable and well-defined compounds, he found to be dissociated again at still higher temperatures, the limits of their formation and destruction both lying within the range of his electric furnace. He was able to prove that the same general laws that regulate the decomposition of ordinary substances at lower degrees of heat prevail with these new compounds at temperatures in the vicinity of 3000° C. In the same way he found that in vaporizing mixtures of metals, such as copper and lead, lead and tin, and copper and tin, the same laws appear, between 2000° and 3000°, as when mixtures of liquids (such as water with alcohol, with ether, and with formic acid), are subjected to fractional distillation at ordinary temperatures. In short, he was enabled to show the unity and constancy of chemical law in the new realm that was thus opened to science, as compared with those already familiar. This result, which he mentions but briefly, though citing several illustrations, is itself of the highest interest, and surpasses in its scope any of his separate discoveries, however novel and valuable.

Prof. Moissan's remarks upon biological chemistry are again highly suggestive. He sums up briefly the body of little-known facts regarding the presence of minute amounts of various metallic elements in many organic structures, both animal and vegetable, where they evidently serve some important functions as yet wholly or almost wholly unknown. In this direction, he recognizes a vast and untrodden field of research. In biology, mineral chemistry and organic chemistry meet. "In fact," he says, "there is only one science of chemistry; all separation is artificial. As energy is one, chemistry is one."

But mineral chemistry, in order to attain to its proper and possible development, must, he urges, be carried out with more exactness and minuteness in the matter of experiment and analysis, than it has heretofore generally received. "It must attain the precision of physics." He cites several striking examples in illustration of this point, and dwells upon it at some length.

The relations of chemistry to astronomy through the spectroscope are briefly alluded to, as showing the unity of chemical law to extend to the farthest visible limits of the universe. Its relations to mathematics, in stereo-chemistry, and the grouping of atoms in space in the molecule, are also touched upon, and some of its more obvious connections with geology, though Prof. Moissan speaks very generally and apparently with no special interest.

As to mineralogy, he says it must rest upon chemical analysis as its foundation, because the species is thus determined. This has been the general view, but there are broad fields of research in geological mineralogy, wherein not merely the composition, but the manner of origin, of mineral species must be considered, and their alterations and replacements under a variety of conditions as yet little investigated. Of these, there is no suggestion or apparent recognition. The artificial synthesis of minerals is referred to more than once, and its great interest fully appreciated. Prof. Moissan would go even farther, and have mineralogy to include not only natural substances, but the countless host of laboratory products. In this view, he is no doubt correct from a theoretical and philosophical standpoint, but how far it may be possible thus to extend the scope of mineralogy practically, is a matter of serious question.

But alas! the grand chemist is no more! How we long, in reading this noble introduction, to see the great work itself, that he had planned and outlined, but was not permitted to complete! It would have marked a new era in mineralogical chemistry, and opened to science a storehouse of treasures, to which he alone had the key.

His last, a posthumous paper on "A Property of Platinum Amalgam,"[6] was read at the Academy of Sciences March 18, 1907, in which he states: "Pure mercury shaken with water, as is well known, forms no mixture with it, but an amalgam of mercury and platinum after being shaken for a few seconds with water forms a semi-solid mass, of the consistency of butter, and of about five times the volume of the original amalgam. This emulsion is stable, and exhibits no change after standing for a year; it resists the action of heat and of cold. Microscopic examination shows droplets of water disseminated through the mass, giving it a cellular appearance. Copper, silver and gold amalgams do not form emulsions with water. Platinum amalgam forms emulsions with other liquids also, such as sulphuric acid, solutions of ammonia, ammonium chloride, sodium chloride, glycerin, acetone, alcohol, ether, carbon tetrachloride, chloroform. All are stable. Emulsification is also produced when mercury is shaken with water to which a 10 per cent. solution of platinum chloride has been added."

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[6] Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. CXLIV, No. 11, March 18, 1907. Chemical News, April 5, 1907.

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A paper read at the Eleventh General Meeting of the American Electrochemical Society, in Philadelphia, Pa., May 2, 1907; President Carl Hering in the chair.

ON THE ESTIMATION OF HIGH TEMPERATURES.

BY GEORGE K. BURGESS.

I propose to give a brief account of the present state of pyrometry, with special reference to the estimation of temperatures above 1,200° C, including some of the methods of measurement which may be employed to determine very high temperatures. Mention will be made of the use of the gas thermometer, the thermoelectric pyrometer, and a description given of the application of certain of the laws of radiation to the measurement of temperature. The determination of fixed points, or reference temperatures, will also be spoken of, especially in the temperature range above 1,200°; and finally a comparison of the temperature scales as determined by recent observers will be given.

The generally recognized temperature scale up to 1,200° C is that of the gas thermometer. This scale is fixed by the determination of certain reference temperatures such as melting and boiling points, and then preserved and distributed by means of pyrometers calibrated in terms of the temperatures of these fixed points. It may eventually be desirable to define temperatures in terms of the thermodynamic scale which is independent of the properties of any particular substance. At the present time, however, the limit of accuracy attainable in gas thermometry, at least for temperatures above 500° C, does not exceed the departure of the gas scale from the thermodynamic scale. The scale as defined by various gases is also practically identical. Thus Jaequerod and Perrot[1], using N, Air, CO, CO_2, and O at constant volume get values for the melting point of gold agreeing to better than 1°, and ranging about 1,067°C. Other determinations of the gold point are 1,064°C by Holborn and

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[1] Jaequerod and Perrot, on the melting point of gold and the expansion of certain gases between 0° and 1,000° C. Comptes Rendus de l'Acad. (Paris), *138*, p. 1,032 (1904).

Day[2], using nitrogen at constant volume; and 1,065°C by D. Berthelot[3] by a method equivalent to the constant pressure thermometer. We may say with considerable positiveness, therefore, that the temperature scale is known to within 5° up to 1,200°C.

It may be of interest to call attention to the precision with which the temperature scale in this interval may be reproduced by means of metals purchased in the United States, in terms of their freezing points. In the following Table I are given some of the results of such a study carried out at the Bureau of Standards. The temperature measurements were made with several thermocouples, and from four to twenty observations were taken on each sample.

TABLE I.

Reproducibility of Fixed Points in the United States.

Source of Metal	Sn	Zn	Al	Sb	Cu
"Kahlbaum"	**232.10**	**419.0**	655	**630.5**	**1084.1**
Eimer and Amend "C. P." . . .	232.03	418.7	656	621	1084.1
Eimer and Amend "Metallic" .	232.17	416.5	. . .	619	
Baker and Adamson "C. P." . .	232.25	418.8	. . .	. . .	1084.1
Pittsburg Reduction Co.	. . .	. . .	658	. . .	. . .

It is evident from the table that, with the exception of antimony, the metals usually employed to fix the temperature scale may easily be obtainable in this country in sufficient purity to reproduce the temperature scale with great exactness.

Above 1,200°C, there is as yet no generally accepted temperature scale, and extrapolation in terms of some phenomenon varying with the temperature must be resorted to. Depending on the phenomenon used, different values will be assigned to the fixed points that may be determined.

Let us first consider the estimation of high temperatures by means of thermocouples constructed of the platinum metals and their alloys. The usual type of thermocouple is a wire of a 10 per cent. rhodium or iridium alloy of platinum joined to a pure platinum wire. The relation between the electromotive force (E) of such a thermocouple and the temperature t of its hot

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[2] Holborn and Day, Am. Jour. of Science, *11*, p. 145 (1901).

[3] D. Berthelot, Comptes Rendus, *176*, p. 473 (1898).

junction, (when the cold junction is kept at O°C) in terms of the gas scale, is usually given as

$$E = a + bt + ct^2 \qquad (1)$$

This empirical relation gives temperatures on the gas scale very exactly in the range 300° to 1,200°C, and has been used to determine fixed points as high as the temperature of melting platinum. Results obtained by extrapolation of equation (1) in this way at the National Physical Laboratory[4], the Physikalisch-Technische Reichanstalt[5] and the Bureau of Standards[6] are given in Table II.

TABLE II.

Thermoelectric Estimation of Melting Points.

	Ni	Pd	Pt
Harker at N. P. L.	1427°	. . . . .	1710°
Holborn and Henning at P. T. R.	. . . . .	1535	1710
Waidner and Burgess at N. B. S.	. . . . .	1530	1706

These results are certainly very concordant although the values for individual thermocouples differ by as much as 20°.

If results with the ordinary thermocouples are expressed in terms of Holman's[7] formula

$$E = mt^n \qquad (2)$$

where m and n are constants, the palladium and platinum melting points become[8] 1,543° and 1,731°C respectively.

Other types of thermocouples, however, such as 90Pt-10Rh, 80Pt-20Rh and Ir, 90Ir-10Ru, give somewhat discordant results[8] when their indications are interpreted in terms of these two formulæ (1) and (2). It cannot be said that there is any particular extrapolation formula which holds generally for different types of thermocouple, so that there is very considerable uncertainty attached to the estimation of high temperatures by thermoelectric means alone.

[4] Harker, Chemical News, *91*, p. 262 (1905).

[5] Holborn and Henning, Berlin Akad., *12*, p. 311 (1905).

[6] Waidner and Burgess, Bull. Bureau Standards, *3*, p. 1 (1907).

[7] Holman, Proc. Am. Acad., *23*, p. 193 (1895).

[8] Waidner and Burgess. loc cit.

We may next consider the determination of high temperatures by radiation methods, of which there are several, based on the relations which have been found to exist between the intensity of total and monochromatic radiation and temperature. Just as the thermodynamic scale of temperature is independent of the thermal properties of any particular substance, but would be exactly reproduced by an ideal gas, and is very nearly realized by the thermal properties of ordinary gases; similarly, the radiation scale of temperature is independent of the radiating properties of any particular substance, but would be exactly reproduced by the radiation from a "black-body," and is very nearly realized by the radiation from an almost completely closed furnace at a uniform temperature. The radiation scale then may be and, in practice, is so defined as to be an extension of the thermodynamic scale. It is realized by measuring the intensity of radiation from an uniformly heated furnace of small aperture. Any other substance than such an experimental black-body will have an apparent temperature, which is characteristic of the substance and kind of radiation, lower than its true temperature, when measured by radiation methods, because a black-body emits radiation of maximum intensity for any temperature. We call *black-temperature* the temperature a black-body would have to give radiation of the same intensity as that emitted by the substance under observation.

The radiation methods most commonly employed are based on the use of light of a definite wave length. Wien's equation expresses the relation between the absolute black-temperature, T, and the intensity, J, of any monochromatic radiation of wave-length λ, as follows:

$$J = C_1 \lambda^{-5} e^{-\frac{c_2}{\lambda T}} \tag{3}$$

In practice we are generally concerned with the ratio of two intensities J_1 and J_2 at temperatures T_1 and T_2, when equation (3) reduces to

$$\log \frac{J_1}{J_2} = \log K = \frac{c_2 \log e}{\lambda} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \tag{4}$$

The value of c_2 depends on the nature of the substance sighted upon, and for a black-body, has been variously taken in recent work from 14,600 to 14,200. The following values, Table III, of the palladium and platinum melting points have been found by sighting upon the melting metal within an electrically heated iridium tube furnace which approximated a black-body.

TABLE III.

Optical Estimation of Melting Points.

	c_2	Palladium	Platinum
Nernst and Wartenberg[9]	14,600	1541°C	1746°C
Holborn and Valentiner[10]	14,200	1582	1789
Waidner and Burgess[11]	14,500	1546	1753

It will be noticed that the differences may in a great measure be attributed to the value of c_2 assumed by the different observers. The value of $c_2 = 14,200$ was found by Holborn and Valentiner to satisfy their optical observations of temperature when interpreted in terms of the indications of a nitrogen in iridium gas thermometer used up to nearly 1,600°C. The uncertainty in the temperatures as given by this gas thermometer may easily exceed 20° at 1,600°. More work must be done before the value of c_2 is satisfactorily determined.

It is evident that the optical scale, however interpreted, gives temperatures considerably higher than does the extrapolation of either of the thermoelectric relations (1) or (2). The following Table IV gives the corrections that should be added to thermoelectric determinations, making use of equation (1) to give temperatures in terms of the optical scale as determined at the Bureau of Standards[12], which latter scale represents "true temperatures" with greater probability than does the thermoelectric extrapolation.

TABLE IV.

Thermoelectric and Optical Scales.

Temperature on Thermoelectric Scale	1200°	1300°	1400°	1500°	1600°	1700°
Optical—Thermoelectric	0	+2	6	14	25	43

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[9] Nernst and Wartenberg, Verh. Deutsch. Phys. Ges., *8*, p. 48 (1906).

[10] Holborn and Valentiner, Ann. d. Physik, *22*, p. 1 (1907).

[11] Waidner and Burgess, *loc. cit.*

[12] Waidner and Burgess, *loc cit.*

It is also possible to make use of the intensity of radiation from the exposed surface of refractory material, as platinum, in order to measure its temperature, when the departure of the substance from ideal blackness has been determined. The relation between the black-temperature using red light and the true temperature has been determined[13] for platinum with considerable precision. The readings of an optical pyrometer sighted on a platinum strip may therefore be interpreted readily in terms of true temperatures. Use may be made of this principle to determine the melting points of substances in very minute quantities.[14]

We may cite as an illustration of this method, the determination of the approximate values of the melting points of the members of the iron group in hydrogen, as carried out at the Bureau of Standards.

A platinum ribbon, heated electrically is enclosed within a cylinder which may be filled with pure hydrogen. A very minute quantity—0.001 *mg* is sufficient—of the metal whose melting point is desired, is placed upon the platinum strip. The current is increased until the speck is seen to melt as observed with a microscope through a mica window. Simultaneously the temperature of the strip is measured by means of an optical pyrometer. The results obtained are given in Table V.

TABLE V.

Approximate Melting Points of Iron Group.

Metal	Purity	Melting Point
Iron	99.95 per cent	1505°C
Chromium	98-99	1482
Cobalt	99.95	1464
Nickel	99.95	1435
Manganese	98-99	1207

A pure oxide of metal may be used if the oxide is reducible by hydrogen. Thus colbalt from cobalt-carbonate and nickel from nickel-oxide gave results identical with those obtained with the metals. The melting point of cobalt would be an excellent

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[13] Waidner and Burgess, loc. cit.
Lummer and Kurlbaum, Verh. Deutsch. Phys. Ges., *1*, p. 247 (1899).

[14] Waidner and Burgess, Phys. Rev., *22*, p. 359 (1906).

temperature to use as a fixed point, as cobalt is relatively cheap, oxidizes but little and its oxide is but slightly soluble in the metal. Its natural impurities *Fe* and *Ni* affect the melting point hardly at all, and the melting point, in contrast to the viscous melting of *Fe, Cr,* and *Mn,* is very sharply defined.

Our knowledge of the numerical values to assign to very high temperatures, *i. e.,* above 1,800°C, is still in the formative stage and no very positive statements can be made at the present time. A beginning has been made, however, in the location of certain temperatures which may eventually be used as fixed points. The only methods here available are those based on the laws of radiation.

Holborn and Henning,[15] using the surface radiation method above described, have found the black-temperatures, using red light, of melting rhodium and iridium to be 1,650°C and 2,000°C, respectively. If these metals had the same emissivity as platinum, which is improbable, at least for iridium, their true temperatures of melting would be about 1,880°C for rhodium and 2,300° for iridium. Nernst[16] has endeavored to find the iridium melting point by determining the total photometric brightness of 1 mm^2 of the melting metal in terms of Hefners and gets, according to the method of reduction,[17] values ranging from 2,200° to 2,300°C.

At the Bureau of Standards,[18] we have made use of a modification of the surface radiation method by means of which temperature measurements of considerable precision may be made, even in the range above 1,800°, and which is applicable to the exact determination of the melting points of any substance which can be manufactured into wire or ribbon and which does not volatilize before melting. We have thus far applied the method to a determination of the selective emission and melting points of tantalum and tungsten, and hope to extend it to the study of iridium, osmium, titanium, and other refractory substances.

The procedure is as follows: The metal is mounted as a filament in an incandescent lamp, and, by sending a current

[15] Holborn and Henning, *loc. cit.*

[16] Nernst, Phys. Zs., *4,* p. 733 (1903).

[17] Rasch, Ann. der Physik, *14,* p. 193 (1904).

[18] Waidner and Burgess, Elec. World, Nov. 10, 1906. Bull. Bureau of Standards, *2,* p. 319 (1906).

through, it may be adjusted to the same brightness as a carbon strip, also mounted in *vacuo*. The temperature of the carbon strip is given by an optical pyrometer. Using red, green, and blue glasses before the metal filament its black-temperatures may be determined as a function of the current. In this way the temperature-current relation for the three colors, and thus the selective emission, may be very exactly determined up to 1,900°C. In general, a substance has an apparently lower temperature for red than for green or blue light, as measured by an optical pyrometer with colored glasses before the eye. True temperatures are approximately obtained by adding to the temperature reading for red light twice the difference between the red and blue temperature readings. Above 1,900°, temperatures are estimated by extrapolation of the current-temperature relation found to hold up to 1,900°C. The melting point is found by increasing the current until the filament melts and noting the current at that instant. In this way the value of the black-temperature, using red light, $\lambda = 0.66\mu$, of the melting point of tantalum was found to be 2,742°C ± 10 from five determinations. This corresponds to a true temperature of the tantalum melting point of about 2,900°C. Similarly the melting point of tungsten was found to lie between 3,050° and 3,100°C.; its black-temperature ($\lambda = 0.66\mu$) was 2,940°.

The use of an electrically heated ribbon mounted in *vacuo* as a radiating source is very convenient for the calibration of optical pyrometers. With a tungsten ribbon to sight upon in place of the carbon, the direct comparison of optical pyrometers might be carried to very much higher temperatures than heretofore, and with a very small expenditure of energy and time. It does not seem improbable that in the near future, when an optical pyrometer is submitted to a standardizing laboratory for test at three points, it may be calibrated at the temperatures of 1,000°, 2,000° and 3,000°C in less than half an hour.

The use of the gas thermometer at these extreme temperatures seems out of the question, at least for some time to come, so that it will be necessary for us to depend on the radiation laws for our definition of the upper ranges of the temperature scale. We have already mentioned the spectral energy law of Wien. Finally, we may call attention to the use of the total radiation emitted by a black-body as a measure of the temperature. The Stefan-Boltzmann law expresses the intensity of total radiation, E in terms of the absolute temperature T, as follows:

$$E = k\,(T_1^4 - T_0^4) \qquad (5)$$

This radiation law has the more satisfactory theoretical basis, but has not been used to the extent that has Wien's law (3) for the estimation of high temperatures. It appears to be much more difficult experimentally to get accurate results using the total radiation method, or the Stefan-Boltzmann law, than when using the spectral radiation method or Wien's law. It is very important that further work be done on the comparison of temperature measurements by means of these two laws. At present we are practically dependent on a very memorable experiment of Lummer and Pringsheim[19] caried out at the single temperature of 2,000°C for an experimental demonstration that the various radiation laws are in accord, although there is some evidence[20] that even at the temperature of the electric arc, about 3,700°C, there is no very great if any discrepancy.

It is evident from the foregoing that, in the field of pyrometry of precision, although much has been done, there is still an almost unexplored region of which hardly a preliminary survey has been made. It is also interesting to note how the technical needs and the scientific pursuit of knowledge in this field are proceeding abreast of each other.

Washington, D. C.

DISCUSSION.

MR. C. A. HANSEN: It strikes me that if Dr. Burgess tries to merge a carbon strip into a metallic filament running under normal conditions of a watt per candle, he will be troubled firstly by an Edison effect which obscures his optical pyrometer, and secondly by the difficulty of securing uniform temperatures throughout his carbon strip. I suggest the use of a tungsten strip in place of the carbon comparison filament.

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[19] Lummer and Pringsheim, Verh. Deutsch. Phys. Ges. (5), *1*, p. 3 (1903).

[20] Waidner and Burgess, Bull. Bureau of Standards, *1*, p. 109 (1904).

Mr. G. K. Burgess: The actual determinations with the carbon strip were made up to 1950°, and the rest of the measurement is exterpolation of the current-temperature relation of the metal lamps. We are indebted to Mr. Howell for making the very uniform carbon strip; it does not vary by 5° over several centimeters.

Mr. Hansen: How about substituting a tungsten strip for the carbon strip?

Mr. Burgess: That we want to do.

Prof. J. W. Richards: I think it is a matter of gratification to see that the doubt that has been cast upon the melting point of platinum by recent tests, has been resolved again. We have been so accustomed to taking the melting point of platinum as 1775°, as being approximately right, that to be told by three authorities that it is somewhere in the neighborhood of 1710° has shaken our confidence in the most reliable scientific data; and I think we have been receiving a lesson not to accept too readily determinations which are new and which may be subject to revision.

I would like to ask whether I understood Mr. Burgess aright, that nickel oxide and cobalt oxide or carbonates decompose spontaneously at the temperature which is used to melt the metals?

Mr. Burgess: The nickel oxide, or cobalt oxide, was put on a soft platinum strip in hydrogen, and, of course, the reduced metal would melt eventually.

Prof. J. W. Richards: I would like to call attention to a mistake which a German correspondent has made in the last issue of "Electrochemical and Metallurgical Industry," concerning fixed points in pyrometry. He has stated that the melting point of tin has been determined accurately at 241°. That is contrary to the facts, for that it is 232° has been known for several years; but to have a man of some standing come out in print and say it is 241°, shows the carelessness with which some people quote these data.

The determination of these high temperatures will be of great importance to electrochemists, as it will be possible to measure accurately the temperature of electrical furnaces; and a great deal of good work and valuable applications of pyrometry will be made as soon as reliable methods are found.

Mr. Burgess, what is to be expected of interference in using optical pyrometers by the metallic vapors which may be found in electric furnaces at high temperatures?

Mr. Burgess: I suppose the presence of those vapors is really the most embarassing phenomenon we have to deal with to-day. It limits the work and the precision of the measurements very greatly.

Dr. C. P. Steinmetz: One of the temperatures given here appears to me rather lower than our experience would indicate—the melting point of chromium. It is given as lower than that of nickel. We find, however, that in a regenerative gas or oil furnace, in which we had no difficulty to rapidly melt down nickel, we could not melt the chromium of the Goldschmidt process and to alloy chromium with other metals we had to melt first the other metals, superheat them to temperatures considerably above the nickel melting point, and then add the chromium, in which case it gradually dissolves in the fused mass. It would appear to me, therefore, that the melting point of chromium is far above that of nickel or iron or cobalt.

Mr. Burgess: This I also questioned most strongly. The early determinations, when we had impure hydrogen, were very much higher and very irregular; but, apparently, when you get rid of the excess of oxides and other materials, the chromium point is fairly definite, and, at least by this method, gave a melt at the temperature indicated.

President Hering: Is it not possible that the hydrogen may combine with the metal to form a hydride, which has a different melting point?

Prof. J. W. Richards: It may be likely that the presence of a small amount of aluminium in this chromium produces aluminium oxide and interferes with the apparent melting of the material. A very small proportion of an infusible oxide will raise the apparent melting point very greatly.

Mr. H. N. Potter: I at one time made a filament of chromium for an incandescent lamp, fairly good chromium, and only reached a point of incandescence with it, so the fusing point must be considerably lower than we have been given to suppose.

Now, in regard to Prof. Richard's question regarding metallic vapors—I had that problem come up some time ago, and I found that you could do it, because you can measure instantaneous temperatures; if you throw into a furnace a blast of inert gas, right in the line of the optical pyrometer, you get instantaneous readings which are tolerably good.

Prof. S. A. Tucker: A current of hydrogen will get rid of the fumes momentarily, but it will not prevent them for any length of time.

A paper read at the Eleventh General Meeting of the American Electrochemical Society, in Philadelphia, Pa., May 4, 1907; President Carl Hering in the chair.

A BOMB CALORIMETER FOR USE WITH SUBSTANCES WHOSE OXIDES ARE SOLIDS.

By Henry Noel Potter, Sc.D.

In attempting to measure accurately the heat of combustion of silicon and of certain silicon compounds, a difficulty is experienced in determining how much silicon is actually burned.

The determination was attempted in a bomb calorimeter of the Berthelot type, wherein the substance is ignited in oxygen under 20 atmospheres pressure, and the heat measured by absorption in a known quantity of water in which the bomb is immersed.

When silicon, even in a state of fine subdivision, is so ignited, it does not all burn, but a protecting film of oxide forms and the combustion ceases without penetrating to the centers of the silicon particles. When there is no other substance present except silicon which can burn, the amount of silicon oxidized can be found by calculation based on the excess of weight of the oxide formed over that of the sample of silicon taken.

For this work, there was available a bomb made by Dinsmore & Singleton, in accordance with the designs of Prof. Atwater, of Wesleyan University.[1]

This bomb consists of a tool-steel cup and a cover of the same material clamped upon it by a steel ring, tightness being secured by a lead gasket. This steel structure is for the purpose of giving sufficient strength to withstand the gas pressure at the time of combustion, which may be considerable.

Within the steel shell there is a lining which consists of a gold-plated copper cup accurately fitting the steel cup, and a nickel lining fitted to the steel cover. An electrical connection is insulately supported from the cover, to which a crucible support is conductingly attached.

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[1] Description of a Bomb Calorimeter and Method of its Use, W. O. Atwater and J. F. Snell. Jour. Am. Chem. Soc., XXV, No. 7, July, 1903.

The material to be burned is placed in a crucible in its supporting ring, and an electrical igniter, consisting of a spiral of fine platinum wire, is buried in the mass, and connected to two contacts, one of which is also the crucible support.

When the cover is in position, the bomb is first pumped to remove the nitrogen of the atmospheric air. This is not usually done in organic combustions, as the hydrogen present unites with any oxidized nitrogen to form nitric acid, which being liquid, remains in the bomb, and can be analytically determined. In the combustion of silicon, however, there is no hydrogen present, and any oxygen burned will remain as a gas, and be lost on releasing the gas pressure from the bomb after the combustion. It is therefore desirable to reduce the nitrogen correction to a negligible amount.

With the apparatus described above, a large number of combustions were made, carefully weighing the sample of silicon, and, after burning, brushing out the residue in the form of a lump of slag and a considerable amount of extremely fine silica adhering to the inner surface of the bomb lining.

This method was not found to give sufficiently concordant results, as it is very difficult, in the first place, to detach all of the slag and silica from the bomb lining without loss, and in the second place it is practically impossible to get constant weight, as the substances and the brushes used gain and lose moisture rapidly and irregularly.

At first, camel hair brushes in quill supports were tried, but these cannot be heated high enough to be thoroughly dried without some disintegration. Subsequently, a rubber "policeman" was used, but this gave no better results, and, after a few experiments with specially-made brushes of fine platinum wire sealed into glass, it was found advisable to alter the construction of the bomb so that the weight before and after combustion could be determined without disturbing the combustion products in any way.

This can be done by modifying the bomb lining so as to make what amounts to two concentric bombs, a thin, light inner one of chemically inert material, and a heavy outer one of steel for strength.

The change consisted in making the lining of the cover of the bomb removable, and supporting the electrical contact and crucible holder on this lining cover instead of on the main cover. The inner cover co-operates with the old lining of the bomb cup to form a completely closed removable bomb lining of such small weight as to permit of its being very accurately weighed on a special balance. Electrical contact was provided for by a stud upon the lining cover contacting with an insulated sleeve upon the steel cover, the other contact being the metal of the bomb itself, as usual.

The advantage of this arrangement is to allow of weighing the sample entirely enclosed in the bomb lining, which is placed as a whole upon one pan of a chemical balance. After weighing, the whole is transferred to the steel bomb, oxygen admitted, combustion effected, gas released, and the lining and contents removed and weighed again without disturbing any of the solids within.

The difference in weight should be the oxygen which has united with the silicon, and from this weight the amount of silicon burned can be readily calculated. This works very well when several further refinements are introduced.

The first difficulty experienced was the blowing of the fine silica into the space between the lining and the bomb. This occurred in two ways—first, through the oxygen port, and second, at the line of contact between the lining cup and the lining cover. The oxygen port was protected by extending it as a tube, and filling the tube with compressed glass wool. Cotton was tried, but the hot gases at the time of explosion ignited it, so that a non-combustible filter must be used. Asbestos packs too tightly, but glass wool was found to work admirably.

The leakage at the junction of the lining cover and the cup was overcome by bringing this junction opposite the lead gasket of the main bomb, so that this gasket automatically seals the bomb and the two parts of the lining at the same time.

The last refinement is in the crucible support, which gave great trouble by burning off. The combustion of silicon gives rise to very high temperatures, and perforates all kinds of metal and porcelain crucibles, the melted mass running down, fusing off the crucible supports, and not infrequently injuring the bottom of the bomb itself, unless care is taken to shield this, which can best be done by a number of thin layers of thoroughly calcined asbestos paper.

Determining the proper material for the crucible gave a great deal of difficulty. Probably fused silica would be the ideal thing, but, in its absence; little cones of mica sewed together with fine platinum wire gave very good satisfaction. Such a mica cone lasts but one combustion, but it delays the falling of the slag, and is without reaction with the silicon.

The support for this cone is best made by three lugs that project ¼ inch or more upward from the plane of the crucible-supporting ring. If these lugs are not used and the cone allowed to rest directly on the ring, this ring, which is made of solid silver, will be destroyed about every second combustion. With the lugs, however, the cone is at a considerable distance above the ring, which can be protected by wrapping with asbestos string, if desired. It is probably better, however, to avoid the use of asbestos close to the combustion region, as it slags with mixed silicates, and this slagging may be accompanied by some liberation or absorption of heat. Silver is used rather than platinum or nickel, as it does not form a silicide.

The only outstanding difficulty with this apparatus is due to its having a large surface, which gains and loses moisture during the weighings to such an extent as to render accurate operation almost impossible during moist weather.

A great deal of the success which has attended the use of this apparatus is due to a specially-made balance furnished by Voland & Son, of New Rochelle. This balance will carry 500 grams in each pan and is accurate to one-tenth of a milligram.

The removable bomb lining complete weighs about 220 grams. The method of procedure is to weigh out a carefully dried sample, place this in the bomb lining, and dry the whole arrangement in an air bath, allow it to cool in a desiccator, and weigh. After completing the combustion, the lining is carefully removed from the bomb, is again dried, cooled in a desiccator, and re-weighed.

In the following table is shown the result of five sample combustions as made in this bomb.

Material. Crystalline silicon free from silicon carbide, ground in a pebble mill, and only such material reserved as remained suspended twenty-four hours in water; this then leached in HCl, aqua regia and HF.aq, dried with alcohol and ether, and then in air bath, and bolted.

Combustion	Amount Taken Grams	Amount Burned Grams	Corrected Rise of Temperature	Heat of Combustion Per Gram
1	.6347	.52016	1.874° C.	7565.5
2	.6850	.51111	1.846° C.	7584.7
3	.6375	.4795	1.749° C.	7658.4
4	.6857	.5307	1.930° C.	7639.0
5	.7496	.5416	1.949° C.	7526.3

Average—7,594.8 calories per gram, or per equivalent, 28.4 x 7,594.8 = 215,692 gram calories at constant volume.

In conclusion, I wish to express my obligation to Mr. Ernest M. Swett for his great patience and care in operating this apparatus.

DISCUSSION.

Mr. C. J. Reed: I would like to ask the author what the ball mill lining was in which this material was ground.

Mr. H. N. Potter: The ball mill pebbles were flint. They contained nothing which was not certainly eliminated by the subsequent leaching. Analysis of the silicon ready for the bomb show it to be 99.6 per cent. pure, the residue being silica and traces of metallic oxides, which cannot give any trouble.

Mr. J. W. Richards: Dr. Potter spoke of the formation of nitrogen compounds and nitric acid from the nitrogen in the bomb. I have found that to be obviated by exhausting the air from the bomb before oxygen is sent in.

Mr. Potter: I mentioned that. The great trouble, however, is that commercial oxygen does contain some nitrogen, except oxygen which is made electrolytically; it contains hydrogen, which is a great deal worse.

Mr. Richards: We should appreciate how important is the heat of oxidation of silicon for metallurgical purposes. There has been considerable uncertainty for the last ten years between two determinations—one, 7,680, and the other practically 6,430 calories per gram, and it has given rise to much uncertainty as to the heat evolved in Bessemer converters and in open-hearth furnaces. I think that this is one of the most important data in thermochemistry to be recently determined, and I congratulate Dr. Potter upon his work.

A paper read by title at the Eleventh General Meeting of the American Electrochemical Society, in Philadelphia, Pa., May 2, 1907; President Carl Hering in the chair.

THE ELECTRO-METALLURGY OF ZINC AND ITS RELATION TO PRESENT PRACTICE.

By Woolsey McA. Johnson.

In a great many ways the metallurgy of zinc is quite unsatisfactory. The losses are high, amounting to between 120 and 180 pounds of zinc per ton of green ore. The labor charge is excessive—two and one-half to three and one-half men-days per ton of ore. The amount of fuel is from 2¼ to 3½ tons of coal per ton of ore. In addition, the use of fire-clay retorts precludes the treating of many ores, because of the corrosive nature of their mineral impurities.

All these commercial and practical facts are due, philosophically speaking, to the fact that the zinc oxide is reduced at 1022°-1060° C., only by an intensely reducing atmosphere, and that its reduction point is 113° C. above the boiling point of zinc. Consequently, roasted zinc ores are reduced in fire-clay retorts holding 50 to 100 pounds of roasted ore, with a large excess of reducing agent, and externally fired.

These circumstances explain the restricted metallurgy, and furnish us a reason why the tremendous advances in smelting of copper ores, iron ores, and lead ores that have occurred in America in the past fifteen years have not been paralleled in the treatment of zinc ores. In short, it is the small size of the unit.

It is the purpose of this paper to present my views on the subject, crystallized from some years of active practical work, both in testing new processes and in the treatment of large tonnages of corrosive ores in the old retort.

Electricity applied to ore dressing.

Of late, there has been considerable practical success in the concentration of zinc ores by electrical means. This success has had the pleasing effect of improving the practice in the old-time water concentration methods. The net result has been that mines once without value have become profit makers. For instance, the mine owned by the company with which I am now connected was offered, four years ago, to the company then employing me for the sum of $50,000. It has since netted to mine owner, ore broker, and smelter companies nearly $1,000,000 in profit, and is now one of the richest mines in the Southwest. This has been due to rapid advance in ore dressing and the improvement in retort practice.

Electromagnetic separators.

The electromagnetic separator has made, in the past ten years, a steady, and often brilliant, advance into the field of the treatment of complex zinc ores. In this country there are many of these machines that are patented, but only four that are proved commercially suitable for a variety of ores. These are the Wetherill, the Dings, the Cleveland-Knowles, and the International. Lack of time and space prevents a description of these. For further information, reference should be made to the report to the Canadian Government on the zinc resources of British Columbia by W. R. Ingalls. This is practically a treatise on modern zinc ore dressing.

The Wetherill was first developed practically for the ores of the Franklin Mine of the New Jersey Zinc Co. Here the ore is first passed through a preliminary water concentration process and dried thoroughly. It is next passed over the "Wetherills," where a separation is effected between the magnetic Franklinite, a complex compound of zinc oxide, manganese oxide, and iron oxide, and the Willemite, the anhydrous silicate of zinc.

The Franklinite goes to the "Wetherill" grate, where, mixed with anthracite slack, it is "blown," and the resulting zinc oxide caught in a bag house. This zinc white, if properly mixed, makes a pigment superior to white lead for many purposes. The clinker from the grates is put through a blast furnace for the production of "spiegel-eisen."

The Willemite (non-magnetic tails) 40-50 per cent Zn, is used in the plant for the production of spelter. A chemically pure zinc is obtained here, sold as the famous "Horsehead" or the "Bertha" brand.

The series of metallurgical treatments is very profitable, due to the fact that the crude ore assays over 20 per cent. Zn.

The large profits made by the New Jersey Zinc Co. are due, in great part, to the neatness of the electromagnetic separation.

In the West, the electromagnetic separator is used in two ways on the complex sulphides:

(1) To separate the magnetic oxy-sulfide of iron made by roasting, at 600° C., pyritic zinc ores.

(2) To eliminate directly the magnetic sulfide of zinc and iron—the so-called "marmatite."

The first way is used quite largely in the Wisconsin zinc field. To its use can be attributed in large measure the opening up of this field as a producer of high-grade zinc concentrates.

The new Wilfley "down-draft" roaster is most efficient for this "magnetizing" roast, and its probable widespread use will have a most beneficial influence in opening up new zinc producers in Colorado and New Mexico.

The pyrites is oxidized to a complex highly-magnetic product. For the magnetic separation of this, a machine of "low intensity" is preferred to the "high intensity" Wetherill. The "Dings" or "Cleveland-Knowles" is preferable, because of lower cost. Undoubtedly the Wetherill could be modified and cheapened for this purpose.

The Wisconsin field is now producing on an average over 1,000 tons of high-grade "Jack" (sulfide ore) per week, and the practical success for these ores of this process is demonstrated. The recovery of zinc is in certain cases well over 80 per cent. I expect this process to have a great effect in the next five years, because the grade of its concentrates is so high, and high-grade material is so important to the spelter plant.

The second method of treating complex sulfides has produced, in the past, large tonnage of zinc concentrates. It is used only at the Empire Zinc Co's mill, at Canon City, Col., and at the "Rowe" mill, of the American Zinc Extraction Co., at Leadville.

Pure zinc sulfide is practically non-magnetic. As the percentage of iron increases, the magnetic properties increase slowly, but finally, at 8 to 12 per cent. Fe, the "black jack" is quite magnetic. By passing ore containing "marmatite" or magnetic black-jack over a machine of high intensity, a product is made analyzing from 37 to 44 per cent. zinc. This is extremely suitable for the zinc smelter, because the iron is practically chemically combined. The iron oxide of the roasted ore effects a "carbon deposition" from the carbon monoxide produced by the reduction in the retort—the same reaction as in the iron blast furnace. This is the reason why "marmatite" concentrates "work" so very easily in the retort.

Direct magnetic separation will not, in my opinion, have such an advance as the other method, because its scope is limited to a narrow class of ores. However, it will often be used preliminary to the other treatment, for the second has iron in the magnetic mineral, while the first has zinc in the magnetic mineral. If the two were combined, there would be a mixing of the values and a poor separation.

Electrostatic separators.

Three of these have been brought to the demonstrating stage, one of the three to a demonstrated success. The "Huff-Dolbear" has had the benefit of the engineering experience of Prof. Elihu Thompson and Prof. Robert H. Richards. The Sutton-Steele-Sutton has been developed in a metallurgical and mining center, hence it has had the advantage of being close to actual concrete operations. Neither, however, has had the test of large scale commercial work in different mines for a long period.

The "Blake-Morscher" was developed earlier, and has now been in practical operation in Colorado, Utah and Montana for four years. Its theory and practice are described in Ingall's report (mentioned above).

Its commercial applications are well illustrated by the treatment in the mill of the Colorado Zinc Co., at Denver.

At this mill, the ore is crushed and sized on "King" screens. It is then passed over Wilfley tables, and three products are made:

(1) Siliceous tailings.
(2) Zinc-iron middlings.
(3) Lead concentrates.

One (1) is rejected; (3) goes to the lead smelter; (2) is then dried and passed over a Wetherill magnetic separator, where the magnetic black-jack is directly eliminated, and sold to a spelter plant as a zinc concentrate.

The non-magnetic tails from this operation are passed over Blake-Morscher machines. An "iron-product," low in zinc, is made, which is sold to the lead smelter for a flux. The zinc product, containing "resin-jack," which does not conduct electricity, and hence is not repelled by the charged rollers, is a zinc concentrate suitable for the spelter plant.

If the first magnetic treatment of the "Wetherills" had not been inserted, the iron product from the Blakes would be high in zinc, and thus unsuitable for an iron-flux for the lead smelter. Besides, the loss in zinc would have been heavy. The treatment at Denver is rather complex, but it is necessarily so.

Summing up the question of electrical methods in the concentration of zinc ores, it can be affirmed that the opening up of the mines of the Rocky Mountains as zinc producers has been in large measure due to electricity applied to ore dressing.

The use of modern methods has stimulated the work in water concentration, and competition of the two methods has resulted in the co-operation of the two methods.

In addition, the flotation processes of Potter and Delprat, in Australia, and Sanders and Elmore, in this country, the "tube concentration" process of McQuestin, the dry process of Keedy-Dietz and Sutton-Steele-Sutton, are all helping the solution of the concentration of complex zinc sulfides, so that to-day there are few mines high in zinc whose ores are not susceptible of concentration at a loss of less than 30 per cent., producing a product at least 40 per cent. Zn, provided intelligent use is made of practical known facts. Applied electricity has been a great factor in this development.

Igneous electrolytic processes.

Let us now proceed to look into the "rationale" of those processes designed to decompose molten zinc and lead chlorides by the electric current.

The Swinburne-Ashcroft process is the most prominent of these. This was invented by two able English electrochemists, for the purpose of treating the famous Broken Hill "middlings." Chlorine was blown through an apparatus similar to small Bessemer converters. This decomposed the metallic sulfides, and formed the resultant chlorides. The gangue floated on top of the molten chlorides. Enough heat was evolved by the reaction to melt the chlorides and distill the sulphur, which was condensed.

The molten chlorides were tapped and passed over molten lead. This decomposed the silver chlorides as follows:

$$2AgCl + Pb = 2PbCl_2 + 2Ag.$$

The reaction was not very sharp, but a rich base-lead bullion was produced.

The lead-zinc chloride, now free from silver, was electrolyzed at a low voltage. This gave metallic lead and chlorine, which was passed through the chlorine Bessemer process. The lead, of course, was cast ready for the market.

No attempt was made to effect a separation of all the lead, but the last fraction of the lead was reduced by molten zinc by simple decomposition as follows:

$$PbCl_2 + Zn = ZnCl_2 + Pb.$$

The chlorides were then granulated and dissolved in water. Copper was precipitated by scrap iron, or H_2S. The manganese and iron were thrown down by chlorine and caustic soda, and the hydroxide filter-pressed and dried. This product could be sold for a cheap pigment.

The solution was then evaporated, dehydrated against a cheap carbon anode, and electrolyzed for the production of chlorine and spelter. The chlorine goes together with the chlorine from the lead chloride electrolysis, and is blown into the converter for a new cycle.

This process has been described confidently as the best solution of the treatment of complex sulfides. Much capital and much scientific skill have been lavished upon it, but it never has had any great commercial success. It is magnificent, but it is not metallurgy. In my opinion, its greatest weakness lies in the fact that a wet process for eliminating the copper, iron and manganese must be used, thus inserting a complicated wet process into a fire process already complicated. Undoubtedly, sometime it will find a niche in the metallurgy of zinc, but it is never destined to revolutionize the treatment of zinc ores, for the plant is extremely expensive, and the process is intricate.

Messrs. Baker and Burwell, in Cleveland and in Montana, have spent considerable time and money on a process quite similar. Instead of using the chlorine converter, they use a revolving drum, and decompose the sulfides by chlorine at 170° to 190° C.; sulfur chloride is formed, which is condensed in water. The product is leached, and a process almost identical with the Swinburne-Ashcroft process is used. This process seems even more complicated than the parent process.

Wet electrolytic processes.

Most of this class of processes originated in the fertile brain of the late Dr. Hoepfner. The ore is usually roasted, and the roasted product leached with chlorine water. The solution was freed from iron, copper, manganese, and then electrolyzed.

Sulphuric acid had been tried as the solvent, but this was useless. With the electrolysis of zinc sulphate, the solution becomes continually more acid, and soon the electrolyte is so acid that only hydrogen is produced at the cathode.

Dr. Hoepfner was quite wise in abandoning sulphuric acid and using chlorine or hydrochloric acid as the solvent. The same general principle was applied by him in his numerous processes on the treatment of nickel-copper ores or mattes. His wet zinc processes have not had much success as yet, nor does it seem likely that they ever will have. In the first place, the leaching of the zinc oxide is far from complete; gelatinous silica is formed, which is mean stuff to handle in the filter press. In addition, much iron is dissolved, and this adds greatly to the expense, both in plant and in treatment.

Brunner-Mond & Co. use the process in a small way in connection with one of their chemical plants. But it enables them to make use of a by-product otherwise useless. Moreover, the spelter produced is practically chemically pure, and is sold in a limited way at a price above the price for common spelter.

There is but little use in describing the countless processes that have followed in Hoepfner's wake. Few of them have any success. Reference should be made to Dr. Guenther's book on electrolytic zinc processes. The processes herein described are but metallurgical curios.

In my opinion, the straight leaching of roasted zinc ores, by sulphuric acid, made at the plant from roasting the ores, followed by evaporation, crystallization of the zinc sulphate, and subsequent calcining of the zinc sulphate for the production of zinc oxide has greater possibilities, with cheap fuel at hand.

Leaching of the roasted ores with caustic soda or ammoniacal ammonium chloride, with the formation of alkaline plumbates and zincates, with subsequent differential electrolysis, is even better, since ferric oxide is insoluble in this treatment, and the silica problem is of a less difficult nature. There are certain chemical, electrochemical, and engineering obstacles that confront the process, but compared to the Hoepfner or the Swinburne-Ashcroft proposition, this one is distinctly promising.

With regard to electrolytic processes in general, the following conclusions are true.

Leaching experiments on a small scale rarely are a good criterion for results on a large scale.

The amount of power used for precipitating one ton of metal is large, and hence the capital outlay for power plant as well as for the leaching plant and power house, is large.

There are many possible impurities in zinc ores that can complicate the leaching and subsequent purification of the solvent; so much as to make success impossible.

Comparing leaching processes with the electric furnace proposition, it may be said that, in general, pyro-metallurgical treatment has given inherent points of superiority over treatment by hydrometallurgical means.

Electric furnace propositions.

This field certainly is attractive, for it uses the same reactions that are used in the present metallurgy, only instead of communicating the heat from the outside through a fire-clay wall, the heat is put inside in contact with the reacting bodies.

While connected with the Orford Copper Co., it was my duty to report on several electrolytic processes for treating nickel ores or mattes. In figuring on these, there always swept before my vision the four little 44-inch x 46-inch brick nickel blast furnaces used in the "alkaline sulfide" separation. These were ridiculously cheap, but put through an enormous tonnage, though the metallurgical efficiency was not very good. But the commercial efficiency was excellent, and the return on capital large.

The same comparison holds between the electric zinc furnace and the old retort. Assuming power from an hydro-electric installation at from $10 to $18 per horse-power year, the capital invested in spelter plant per ton of ore would be very low. An electric furnace of the "resistance" type, where the charge carries the current (and not of the arc type) will put through an enormous tonnage per cubic foot of active space.

The labor charge, high in the present spelter plant, will be low in a continuous electric furnace.

As the temperature will be under absolute control, the recovery of the metal will be high. The corrosive nature of certain zinc ores should not bother us, for we can use suitable refractory linings or water cooling in a large furnace.

Thus, certain classes of ore can be used in the electric furnace such as are not now amenable for treatment.

The zinc made in a large furnace will be pure and uniform, quite the contrary of the present practice. A thermal efficiency of 85 per cent. can be counted on if the units are of 700 horse-power.

If gas engines were used to generate the power, the thermal efficiency of 85 per cent. times 23 per cent., or about 19.5 per cent., is a fair estimate.

This figure is far higher than the present thermal efficiency of 4 to 6 per cent. in American practice, and 8 to 10 per cent. in European practice.

In this connection it might be noted that the thermal efficiency of the old retort is very high at first, when the charge is of maximum reductivity. At the end the efficiency is low. Roughly, in a Kansas natural gas plant the first two-thirds of the spelter is made with one-third of the gas. Thus the first efficiency is about four times the last efficiency. In my opinion, it is even better than this, and about 15 per cent. absolute.

In my electric furnace work, I worked along this idea, and combined a "pre-heater" with an electric furnace. The first easy reduction was done by indirect heat, and the last and hard by the electric heat. This certainly is beautiful from a philosophical standpoint. There are certain great mechanical and metallurgical difficulties, but these solved themselves.

At present engineering and mining work keeps me so much in the field that it is not good policy for me to push my electric furnace, especially as it is not yet the psychological moment in the zinc business for such an enterprise.

Condensation.

The great problem from a metallurgical standpoint is the condensation on a large scale to metallic molten metal (the redundancy is needed for emphasis), and not to dust or "blue powder."

This has been the snag against which almost all have run. Undoubtedly, there has been much inaccurate knowledge of the real conditions requisite for this. I have laughed at many of my crude first attempts, after now having diagnosed, in operating the old-style retort furnaces, the causes for ailments. Still, I did with a poor condenser condense 150 pounds of metal direct with less than 100 pounds of blue powder.

One of the greatest troubles from an engineering standpoint is the danger of exploding the zinc vapor and carbon monoxide. But I have succeeded in preventing this by means of certain safety devices. One of my improved condensers is embodied in a recent patent.

I have given in a rough way certain ideas about the electric zinc furnace. Let me crystallize the advantages as follows:

(1) Purer and more uniform product.

(2) Higher recovery of zinc, certainly over 95 per cent.

(3) Wider range of ores that can be treated.

(4) Lower labor charge as units are enlarged.

(5) Higher thermal efficiency.

(6) Recovery of lead, copper, silver, and gold values.

(7) Decreased capital outlay when combined with a "preheater," or where power is rented.

The great trouble is the regulation and cleaning of the condenser, and the commercial and metallurgical difficulties inherent in any new process.

I will now epitomize several of the other attempts to treat zinc ores in the electric furnace. There are many of these, but I have selected some typical of the best.

Brown and Oersterle have experimented with a "resistance" electric furnace. They used coal or coke and raw ore and lime.

The lime acted as a desulfurizer. As roasting is done in Kansas at a cost of less than 50 cents for labor and repairs in machine kilns, not much is saved. Besides, often an acid works is operated in conjunction with a spelter plant. This is, in places of acid consumption, a source of $1.25 to $2.00 a ton net financial advantage.

They also attempted to make calcium carbide as a by-product. As this operation requires a temperature of 1600° C. to 1900° C., while zinc reduction requires a temperature of 1022° to 1350° C., this is unwise. Besides, the carbide would be full of impurities, unless the highest grade of Joplin ore were used. However, their work was a first-class contribution to our knowledge of the metallurgy of zinc.

Mr. Frederick T. Snyder, an experienced metallurgist, has attempted to reduce in a Siemen's electric zinc furnace roasted lead-zinc ores. He produces in one operation zinc vapor, lead base-bullion, and a slag. This is a rather bold attempt to do two things at once. But Snyder has forged ahead with the idea that he could at least collect his zinc as blue powder, and then turn it into the spelter in the old retort. He will undoubtedly succeed in condensing a part of his metal, for this is not impossible, even with his adverse conditions. Mr. Snyder's work has my warmest admiration, for it is founded on good common-sense ideas.

Mr. Gustav de Laval has worked out an electric zinc furnace of the "arc" type. In my opinion, the "arc" type is not as good as some modification of the resistance type. The fact that the source of heat in arc-type operation is some distance from the charge, while in the resistance type heat is generated exactly where needed, is a sufficient reason. De Laval is a fertile and able inventor and has had fair success, having actually reached the commercial stage. On low-grade ore he was badly "jarred," as we all have been, in the condenser. Finally, working his furnace on zinc skimmings from the galvanizer or on low-grade leady spelter (94 per cent. Zn.), he produced a high-grade spelter, 99.95 per cent. Zn., which mixed with copper made a cartridge brass. Such a spelter sells for 2 to 4 cents above the market, for this "cartridge test" is the hardest test to which any spelter can be subjected.

De Laval has made in this way considerable high-grade spelter at a profit, the best criterion of a new process. He has now modified his ore process, and uses a reaction something similar to the reaction used on the Wetherill grate by the New Jersey Zinc Co. The roasted ore and coal are blown into a furnace in a whirl, and the lighter products are drawn off from the sides, while heavier are drawn off in the center. Just as Wilfley, in his new roaster, uses a Wilfley motion in his discharge, so de Laval uses centrifugal force in this furnace. The inventive mind always works in its own peculiar sphere of activity. De Laval uses this high-grade zinc oxide (70 to 80 per cent. zinc) in his electric furnace for the production of spelter. He thus follows a general principle clearly impressed upon my mind by my former employer, Col. Robert M. Thompson, who was an extremely brilliant metallurgist, as well as an able business man. This is to the effect that electricity is an expensive agent, and thus should be only used on a high-grade product, produced from the ore by some cheap smelting process.

De Laval's various processes are controlled by a strong German metal and banking house, and I believe that his ideas will, in the course of the next few years, work out on a large scale into demonstrated successes. In this connection, it might be noted that the Wetherill process could be used, if modified rightly, for the same purpose. The New Jersey Zinc Co., in fact, does this to some extent. The zinc oxide so formed could also be mixed with coal and charged into the old-fashioned zinc retort. However, zinc oxide is a hard proposition to turn into spelter, unless experienced furnace men are available. The blast furnace can also be used for the purpose of making zinc oxide. Such a process used this way, to produce a high-grade product to be treated in the zinc retort, has great possibilities, and once worked out on proper lines would be a serious competitor of any new process. The process thus applied is analogous to the "copper matting" process in copper smelting.

I look for this operation in the future to be one of the paths of least resistance in the progress of the metallurgy of zinc. It is really a "concentration" process.

Possibilities in the old retort.

The old retort, of course, has certain definite limitations prescribed by the nature of fire clay. It is not decrepit, but at present is enjoying a green old age.

It has, however, certain lines of possible development. I am greatly in favor of larger retorts. The plant which we will build will have retorts holding 60 pounds (possibly 70 pounds of ore later), instead of the 50 to 55-pound ore retorts as used in Kansas. It is possible to modify the Silesian practice to American conditions of cheap coal and high-priced labor, and even use a muffle of 200 pounds or 300 pounds capacity. Silesian muffles carry, to-day, 200 pounds of ore. They would make considerable blue powder, and if sufficiently large could be used simply for the production of blue-powder to be turned into zinc by re-distillation. This, again, is a "concentration" process, as is the blast furnace and Wetherill process.

This would allow of mechanical charging as used in the gas retorts in municipal plants. It would also allow of making a "divided charge" and putting the non-corrosive ore on the bottom of the retort. An inclined retort could be used.

There is a gradual growth of this sentiment among zinc men, but, of course, in this busy time, when everybody is making money with the old retorts, changes will be delayed for some time. Let it be distinctly stated, however, that any inventor who counts on the old figures of 140 pounds to 160 pounds zinc lost per ton of ore, and a smelting charge of $10 to $14 per ton of ore, will run a great risk of mistaking the powers of his supposedly feeble and old competitor.

I have thus concluded a survey of the lines along which electrical methods are likely, in my opinion, to be applied to the smelting of zinc ores. Necessarily, my paper has been general in nature, and, of course, faulty. It is, however, the result of some years' active work in the treatment of zinc ores, and expresses my views on this most fascinating field of metallurgical endeavor.

A paper read at the Eleventh General Meeting of the American Electrochemical Society, in Philadelphia, Pa., May 3, 1907; President Carl Hering in the chair.

THE ACTION OF CARBON ON MAGNESIA AT HIGH TEMPERATURES.

By Oliver P. Watts.

The advent of the electric furnace has caused a demand for refractory materials of a higher order than those formerly employed. Carbon, carborundum, siloxicon, magnesia, and alumina are proposed, or already in use, for electric furnace construction. Of these, carbon is easily the first, in point of resistance to extreme heat, but its oxidation, its high conductivity for heat and electricity, and the avidity with which it combines with most of the metals, unite to prevent its exclusive use for such purposes. Carborundum is next to carbon in resistance to heat, is a poorer conductor, and oxidizes much less readily than carbon, but, like it, combines with metals at very high temperatures. Siloxicon promises to be a valuable refractory material as soon as it can be obtained in the form of bricks, or of sheets of sufficient strength for use.

Of carbon-free refractory materials, magnesia is the most important. It is more refractory than alumina, chromite, or lime, is not so readily attacked by fused oxides, and is not changed to carbide when heated to high temperatures in contact with carbon. Concerning the latter point, Moissan said (Traité de Chimie Minerale, Vol. 3, p. 955; Electric Furnace, p. 240, Trans. by V. Lenher):

"This explains why it is possible to fuse magnesia and bring it into a liquid state in a carbon crucible without reduction of the oxide. At the melting point of magnesia, magnesium carbide cannot exist."

In August, 1905, when the writer was employed in the preparation of iron alloys, under a grant from the Carnegie Institution to Prof. C. F. Burgess, a curious phenomenon was observed. It has only recently been investigated, and forms the subject of this paper.

One of the many varieties of electric furnace experimented with for the purpose of melting iron and forming the alloys consisted of a granular carbon resistor in walls of magnesia brick, with crucibles standing on a graphite shelf just above the resistor. Although the iron was melted by this arrangement, an unexpected difficulty was encountered in the apparent vaporization of the resistor. In an hour and a half after starting the furnace, more than half the resistor had disappeared, and the interior walls of the furnace were coated with a black, soot-like crust to the depth of ½ inch. This was thought at first to be due to impurities in the material of the resistor, so Acheson graphite was substituted for the granular carbon, but with the same result. Crushed coke and arc-light carbons were also tried, but without improvement. The resistance increased as the resistor became more and more attenuated, until the maximum pressure available—100 volts—failed to maintain sufficient energy in the furnace to heat it properly. In one case, the resistance increased in twenty minutes from a minimum of 0.19 ohms to 2.10 ohms. The rate of formation of the black deposit in the furnace increased with the temperature.

At a cursory glance, this phenomenon appeared to be a distillation of carbon, and a consideration of the energy density supported this view. The dimensions of the resistor were 13 x 2½ x 2 inches. The maximum energy used was 66 K.W., or 1,035 watts per cubic inch of resistor. A carborundum furnace, with a resistor 14 feet long and 21 inches in diameter, using 1,000 horse-power, would have an energy density of only 3.2 watts per cubic inch, provided no current passed outside of the core. As this furnace had proved useless for the preparation of iron alloys, it was abandoned for other types, the wasting away of resistor and the formation of the soot-like deposit being ascribed to distillation of the carbon by the extremely high energy densities used.

Since that time, the same phenomenon has been noted by others. H. M. Goodwin and R. D. Mailey (Tr. Amer. Electrochem. Soc., 1906, Vol. 9, p. 90), when endeavoring to prepare fused magnesia in a carbon tube, observed that a black product condensed in the cooler part of the tube. It was found that this was not a carbide, but its chemical composition was not ascertained.

What is the nature of this curious action? That this is not a case of the simple distillation of carbon is indicated from its occurring only in the presence of magnesia. Is the magnesia a catalytic agent for the distillation of carbon? The writer has observed that not only is a block of carbon corroded by contact with a fragment of magnesia, but a smooth surface of the latter is deeply pitted by contact with a bit of hot carbon. There is, then, some reaction between carbon and magnesia. The visible black product would seem to exclude the idea that the reaction is a simple reduction of the magnesia by carbon, and the failure to find a carbide, together with Moissan's experiments in decomposing an impure magnesium carbide by heating it in the electric furnace, would seem to show that a carbide of magnesium has not been formed at any stage of this reaction.

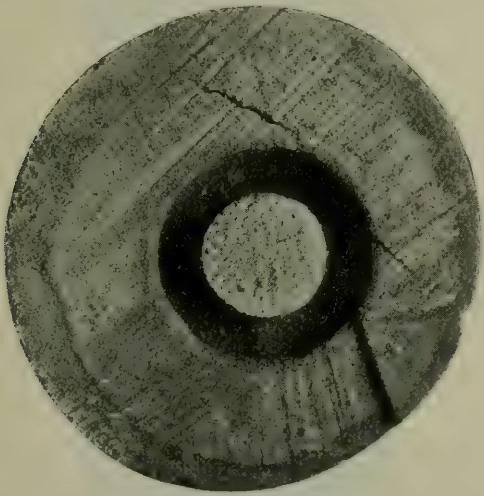

FIG. 1.

A sheet of graphite corroded to the depth of $\frac{1}{8}$ inch by contact with a tube of magnesia.

Recently, experiments were undertaken by the writer to clear up, to his own satisfaction at least, this puzzling behavior of carbon and magnesia in the electric furnace. The first question was to find the relative weights which act upon each other. For this purpose, a weighed amount of electrically-shrunk magnesia was placed in a weighed and covered crucible of

Acheson graphite; this was placed inside a larger, covered crucible, and buried in a resistor of granular carbon, where it was heated two and a half hours, with an average of 37 kilowatts. The experiment was afterward repeated.

	Time Min.	Average Energy K. W.	MgO taken	Loss grams	MgO %	Loss grams	Graphite %
1	145	37	106 g.	34.8	76.9	13.4	23.1
2	55	32.2	25.117	6.294	75.6	2.18	24.7

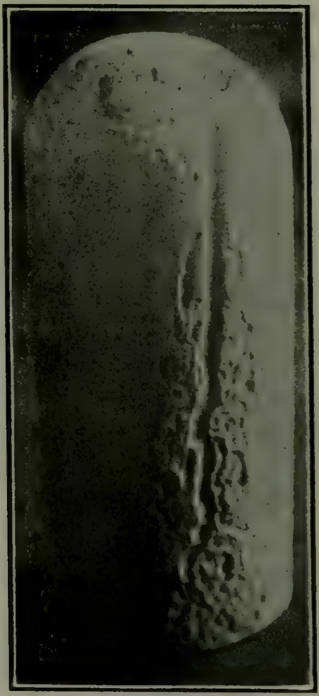

FIG. 2.

A magnesia lining corroded by the iron which distilled out of it and absorbed carbon.

The molecular weight of magnesia is 40.36. In Experiment 1, each 12 grams of carbon carried away with it 40.14 grams of magnesia; in Experiment 2, 35.54 grams. Losses due to oxidation of the carbon by the air originally inclosed in the crucible would lower the observed ratio below that in which the substances really react. This accounts for the low ratio of loss of magnesia in the second experiment, for this loss by oxidation would be nearly the same in both cases, but because of the small weights employed in Experiment 2 the percentage of error is largely increased.

The next problem was to determine the composition and cause of formation of the black product. For this purpose, a mixture of graphite and electrically-shrunk magnesia was packed around a carbon rod 5 inches long and ¼ inch in diameter, and heated for two minutes by 25 K.W. The product condensed on a water-cooled copper tube as a firm black coating, 2 mm. thick. Water proved to be without action upon this. In hot dilute hydrochloric acid it kept its original form, but became a deeper black, and much magnesium chloride was found to be in solution. When free from iron, this action occurred without evolution of gas, Ignited on platinum over a blast lamp, it lost in weight and turned white. Quantitative results are as follows:

	Loss on ignition in air	MgO	Fe_2O_3
1	20.9%	77.3%	1.4
2	21.3%	74.6%	—

Treating by hydrochloric acid, collecting the insoluble black residue and igniting this, the results are:

	Loss	MgO	Fe_2O_3
3	23.2%	—	—
4	22.93%	75 82	1.71

Whether ignition occurs before or after treatment by hydrochloric acid, the loss of weight is approximately the same. Analysis of the product indicated carbon and magnesia in the proportion in which they were found to react with each other.

The next question was whether this black substance is a compound or a mixture. It is uniform in appearance, even under the microscope, and is of considerable tenacity. No physical means have been found of separating it into magnesia and carbon. Its heat of combustion from two determinations in a Mahler bomb-calorimeter was 8,265 and 8,267 calories per gram of carbon burned. Combustion was not quite complete in either case, and in view of the uncertainty introduced by the corrections made for incomplete combustion, the value obtained is fairly close to the heat of combustion of a gram of amorphous carbon, 8,080 calories. An exact agreement would lead to the conclusion that it is a mere mixture of magnesia and carbon.

If it is a compound, it must have the composition indicated by the formula MgCO, or some multiple of this. The heat of combustion for a gram molecule of this is deduced from experiment as follows: Weight of substance taken, 1.6206 grams; residue, 1.2791 grams; loss, .3415 gram. Calories, 2,823; calories per gram of carbon burned, 8,267. Further loss on igniting the residue in air, .0155 gram; total loss, .3570 gram. Hence the weight of the original substance burned in the bomb is 1.5483, the calories per gram of original substance is 1,823, and the calories for 52.36 grams is 95,466. The equation for its combustion as the compound MgCO would be:

$$MgCO + O_2 = MgO + CO_2 + 95{,}740 \text{ calories.}$$

Since the heats of formation of magnesia and carbon dioxide are 145,500 and 97,000, respectively, this would require for the substance, if a compound, a heat of formation of about 147,000 calories. So high a heat value for the product does not, in the writer's opinion, agree with the nature of the reaction between magnesia and carbon. Reaction begins at a high temperature, is very moderate at the outset, and becomes more rapid only by increase in the temperature of the furnace, which would seem to indicate that heat is absorbed, not evolved, by the reaction. This requires that the product or products possess a less, instead of a greater, heat of formation than magnesia.

By grinding in a ball-mill 23 parts of graphite and 77 parts of magnesia, a mixture results which, in physical and chemical properties, is like the product of the electric furnace.

Several later preparations have shown considerable variation in composition:

	Carbon	Magnesia
A	34.36 34.82	65.74 64.66
B	46.09	53.88
C	38.34	—

These had the same properties as the earlier products, and were made in the same way, except that the graphite used was passed through a 100-mesh sieve. The higher carbon content is probably due to graphite carried over mechanically by the more vigorous reaction, resulting from the use of finely-divided graphite.

What is the *modus operandi* of the evaporation and condensation of this carbon and magnesia? Alone, neither vaporizes, except to a trifling extent, at the temperatures attained in the furnaces. The writer offers the following explanation: The reaction $MgO + C = Mg + CO$ is a reversible one under the different temperatures existing in the hottest and the coolest portions of the electric furnaces used. At the higher temperature, the reaction is endothermic, proceeding from left to right of the equation, and producing a mixture of magnesium vapor and carbon monoxide, while at some lower temperature, probably slightly above the upper limits of temperature attainable by combustion processes, the reverse exothermic reaction occurs, and magnesium burns at the expense of the oxygen of the carbon monoxide, producing a mixture of magnesia and carbon. When a furnace is extremely hot, this reverse reaction cannot occur inside the furnace, and the mixture of magnesium vapor and carbon monoxide burns in the air, producing the dazzling light frequently observed. The solid product collecting on the bricks of the furnace is pure white, provided the magnesia is free from iron.

Whether the black substance be a compound or a mixture, the writer has shown that it is chemical action, not a low melting or boiling point, that prevents the use of magnesia in contact with carbon at extremely high temperatures. In ignorance of this important fact, the writer once gave much time and experimentation to the attempt to melt tungsten without introducing carbon, while using magnesia linings in graphite crucibles. The linings failed at the temperature at which the tungsten became plastic, but before it was fully melted. As parts of the linings were missing and that which remained had not been liquefied, the writer came to the incorrect conclusion that magnesia sublimes at high temperatures.

Thinking that a current of hydrogen might so separate the carbon monoxide and magnesium vapor that their reaction with each other would be partially prevented, and that metallic magnesium might be obtained, a mixture of magnesia and carbon was heated in hydrogen, in a carbon tube furnace. No magnesium was found. The product was an extremely fine powder of a uniform light slate color. It had a distinct odor, like acetylene, and decomposed water with evolution of a gas and formation of a white solid. It appeared to be a carbide of magnesium, but sufficient amounts of it for analysis and a study of its properties have not as yet been prepared.

In making iron alloys in the electric furnace, the crucibles used were lined with magnesia, to prevent contamination of the alloys by carbon. These linings were always baked in the crucible before putting in the charge, and as a result of this baking a curious corrosion of the outside of the lining was often produced. It was usually confined to one side, and is well shown in the accompanying photograph, Fig. 2. It is evident that some liquid, very corrosive toward magnesia, had trickled down between the lining and the wall of the crucible. In such cases of corrosion, the lower part of the crucible always contained highly-carbonized iron, either sticking to the walls in solidified drops, or collected in the bottom. The source of this iron was the magnesia used to form the lining, for this contained about 7 per cent. of oxide of iron, and was therefore brown in color. When baked to a very high temperature, the linings became white, and contained but a trace of iron. Heated to lower temperatures, the color of the resulting linings was darker, and they were slightly, if at all, corroded on the outside. When linings were made from magnesia that originally contained no iron, or that which had been once baked in the electric furnace until white, there was no corrosion, and the crucible was free from carbonized iron. The action then appears to be as follows: When the temperature is high enough, iron oxide vaporizes, and coming in contact with the walls of the crucible, is reduced, collecting as microscopic spheres of iron. These grow in size until large enough to flow downward under the influence of gravity, when the flowing drop grows by absorption of those with which it collides. As the iron flows downward, it takes up graphite from the crucible until saturated, and vigorously reduces the magnesia wherever it touches it.

To test more fully this corrosion of magnesia by a carbonized metal, holes 11/16 inch in diameter were bored in a block of graphite; weighed amounts of copper, tin, nickel, chromium, and iron were put into different holes, electrically-shrunk cylinders of magnesia were placed on top of the metals, and one magnesia cylinder put in a hole containing no metal. The block was covered by a sheet of graphite, buried in a granular resistor, and heated. The results of several experiments were as follows:

		Cu	Ni	Cr	Fe	C	Sn	Time min.	Average energy
1	Metal	6 g	6 g	6 g	6 g		6 g	50	26 K.W.
	Magnesia	15	15	15	15		15	—	—
	Loss	2.3	3.7	10.7	3.3		7	—	—
2	Metal	10.54	10.50	10.50	10.53	—	10.50	40	25
	Magnesia	6.79	6.72	7.7	7.25	7.01	6.06	—	—
	Loss	0.10	1.84	0.72	.35	.01	.06?	—	—
3	2 continued		—	—	—	—		110	34
	Losses		4.88*	6.69*	6.90*	1.64		—	—
		Cu	Siloxicon	SiC	Fe	C			
4	Magnesia	6.2332	8.0445	8.0709	7.9642	6.1430		80	23
	Loss	1.1501	8.0445*	6.0000	7.9642*	1.4150		—	—

The losses marked thus "*" indicate that all magnesia had disappeared. The interior dimensions of the resistor furnace used were 18 x 5½ x 7½ inches. These results show that several carbides reduce magnesia far more rapidly than pure carbon does. As was anticipated, copper and tin had but slight, if any, action as carriers of carbon to the magnesia. For vigor of action, the order of the substances tried is as follows: Siloxicon, chromium, iron, nickel, carborundum, carbon, copper, tin. The magnesia adhered firmly to the copper and tin, but to none of the other materials.

The results of these experiments are briefly stated in the following summary:

1. At extremely high temperatures, magnesia and carbon react rapidly, and in a closed vessel a solid black product results.

2. Reaction occurs according to the equation $MgO + C = Mg + CO$.

3. This reaction is reversible, and at a lower temperature reforms the magnesia and carbon as an intimate mixture.

4. Magnesia containing iron oxide in large amount may be freed from this impurity by heating strongly in an electric furnace of the resistance type.

5. Magnesia is reduced more rapidly by certain carbides than by pure carbon. The carbides of iron, nickel, and chromium are

particularly active in this respect, as are also siloxicon and carborundum.

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DISCUSSION.

Dr. J. W. Richards: I think the explanation given by Mr. Watts is correct, because the compound MgCO in such case would be analogous to magnesium carbonyl and would probably, as such, be a gas at temperatures above a low red heat, and liquid below that, and therefore it is an improbability that this could possibly be a compound of the formula MgCO.

Secondly, we all know that silicon, aluminum and magnesium can reduce CO at the temperature of molten steel; therefore, the reverse reaction, the reduction of CO by magnesium itself at the temperature of the furnace, is very probable, and the reduction of magnesia more actively by carbon dissolved in the iron than by carbon itself, is quite in line with what is observed in the blast furnace, where large quantities of silicon are reduced, not by the carbon, but by the carbon dissolved in the iron, which is the only rational explanation of the presence of such large amounts of silicon as are found in the pig iron. The observation of Mr. Watts is quite in line with this well-known phenomenon of blast-furnace practice.

Mr. Reed: It seems to me that we could explain that in this way: That magnesium carbonyl is formed at a certain temperature, and that in a gaseous state is conveyed to another portion of the tube, and there the carbon reduces. The carbon is set free, and the oxygen is taken by the magnesium. That would also explain the fact that the substance has a calorific power equal to that of carbon.

Dr. W. D. Bancroft: I supposed that the formula for nickel carbonyl was $Ni(CO)_4$, so I really don't see why this should be classed as magnesium carbonyl.

Dr. H. E. Patten: I have done this in a vacuum furnace and with temperatures high enough, and if there is sufficient space for the magnesium to get away, it deposits as magnesium, and you will get this black body right where the magnesium deposits. As carbon monoxide is stable at high and not stable at low temperatures, it seems reasonable to suppose that the reaction goes one way at high temperatures, and on cooling down the reaction reverses.

PROF. C. F. BURGESS: Dr. Watts has credited to various other people the discovery of this point. He does not claim that he discovered this as a new phenomenon.

A paper read by J. W. Richards at the Eleventh General Meeting of the American Electrochemical Society, in Philadelphia, Pa., May 4, 1907; President Carl Hering in the chair.

ON THE ELECTRICAL REDUCTION OF TITANIFEROUS IRON ORES.

BY GUSTAVE GIN.

Titaniferous iron ores are found in many places, at times in such quantities that their utilization in the metallurgy of iron might be very profitable. Besides *Ilmenite,* the known deposits of which are not extensive enough to be worked on a large scale, there exist large deposits of iron minerals containing titanic iron ore concentrated by nature along with magnetite. Such deposits are found in Norway, Sweden, the United States and Canada, in considerable abundance, in the form of black sands. They are likewise found on the coast of the Island of Santiago, among the Cape Verde islands, and on the southern coast of Java. They can be easily enriched by electro-magnetic concentration.

Such black sands, and the concentrates from them, are but little used in the metallurgy of iron, although their purity and freedom from phosphorus and sulphur ought to make them desirable. It seems that this indifference is based on the opinion that the titaniferous slags resulting from their use are difficultly fusible in the blast-furnace.

It is possible that this difficult fusibility of titaniferous slags is caused by an improper calculation of the charge of the furnace. To form a uni-silicate calcium slag requires approximately as much lime as there is silica to be fluxed, but a uni-titanate calcium slag requires only two-thirds as much lime as titanic acid fluxed. It is possible that too much flux is ordinarily used when titanic acid is present with silica in the furnace. Whether this be the fact or not, there is no difficulty in fusing silico-titanate calcium slags in electric furnaces.

In 1901, I treated in an electric furnace titaniferous iron ore from Norway of the following composition.

$Fe^{3}O^{4}$	55.73	per cent.
$Fe^{2}O^{3}$	3.16	“
$TiFeO^{3}$	30.90	“
$Si^{2}O^{3}$	0.56	“
$Al^{2}O^{3}$	3.61	“
Not determined	3.61	“

Fe = 53.76 per cent.
TiO^{2} = 16.40 per cent.

The charge was composed of:

Ore	100	kilos.
Limestone	15	“
Coke	25	“

and 274 kilograms was treated in 4 hours, using 286 kilowatt-hours of electric energy, and yielding 102 kilos of metal of the following composition:

Iron	94.60	per cent.
Carbon	3.10	“
Silicon	0.86	“
Titanium	0.10	“
Phosphorus	0.06	“
Not determined	1.28	“

The slag had the following composition:

TiO^{2}	32.50	per cent.
SiO^{2}	20.80	“
$Al^{2}O^{3}$	4.10	“
FeO	8.10	“
CaO	32.70	“
Not determined	1.80	“

The electric energy amounted to 2,850 kilowatt-hours per ton of pig iron. In a larger, improved furnace this figure would be certainly not over 2,280 k. w. hours.

The above test was made at the electrochemical plant at Jessains, Department of Aube, France.

Another experiment was made of a similar character towards the close of 1906, with titaniferous concentrates from Java. On December 12, 1906, Messrs. W. Borchers, L. Petitalot, G. Van

Musschenbrock, J. J. Loke and the writer, assembled in the laboratory of Prof. Borchers at the Technical High School in Aix-la-Chapelle, made the following test:

Sandy iron concentrate from Java was mixed with limestone and carbon in the proper proportions, and submitted in a resistance electric furnace to a direct current of about 500 amperes, at a working tension of 60 to 65 volts. The charge was easily melted; at the end of an hour's running the temperature of the melted mass, taken by a Wanner pyrometer, was a little over 1,900°C. The slag and metal were then cast, the metal in a previously-heated crucible; the slag was very fluid and ran easily from the furnace. The clean ingot of metal weighed 42.62 kilos. The slag was black, with glassy lustre.

The analysis of materials and products were as follows:

ORE.			METAL.			SLAG.		
FeO	28.50	per cent.	Fe	94.94	per cent.	SiO^2	8.90	per cent.
Fe^2O^3	49.95	"	Mn	1.52	"	TiO^2	38.72	"
MnO	0.98	"	C	3.05	"	Al^2O^3	5.18	"
CaO	0.37	"	Si	0.37	"	FeO	10.03	"
MgO	2.35	"	P	0.11	"	CaO	34.80	"
TiO^2	16.00	"	S	0.01	"	Etc.	2.37	"
SiO^2	1.60	"	Ti	Trace.				
Etc.	0.25	"						

The pig-iron was very low in sulphur, while the phosphorus it contained came mostly from the carbon used for reduction.

The conclusion drawn from these experiments is that the reduction of titaniferous iron ores in the electric furnace presents no special difficulties, and that pure iron can be obtained commercially therefrom in regions where the ore is near abundant and cheap water power.

(Translated by J. W. Richards.)

DISCUSSION.

PROF. J. W. RICHARDS: The gist of this paper of Mr. Gin is that the experiments which he has made (one in Norway, in 1901, and more recently, December 12, 1906, at Aachen) on the reduction of titaniferous iron ore in the electric furnace, show that from titaniferous ore containing up to 16 per cent. of TiO_2

there was obtained pig-iron which contained only a trace of titanium; and slag, which contained up to 38.7 per cent. of TiO_2, which was perfectly melted at the temperature of the electric furnace, the temperature being measured, by a pyrometer, at about 1900° C. This shows the possibility of producing from this titaniferous iron ore pig iron which is practically free from titanium and containing only 0.01 per cent. sulphur, and, therefore, again draws our attention to the possibility of using the titaniferous ore, such as is found in the Adirondacks, for instance, as the source of a high quality of pig-iron.

A paper read at the Eleventh General Meeting of the American Electrochemical Society, at Philadelphia, Pa., May 4, 1907, President Carl Hering in the chair.

A CLOSED ELECTRIC FURNACE FOR REDUCING AND DISTILLING METALS FROM THEIR ORES.

By Edward R. Taylor.

The very satisfactory working of the closed electric furnace for the manufacture of bi-sulphide of carbon has led to a study of possible application of some of the principles so useful there in other directions. The volatile metals seemed to offer a good field for such study.

The loss of heat by radiation is a large factor in most furnace operations, but the ready fusibility of sulphur made very practical and easy the saving of much of this heat in the bi-sulphide of carbon furnace, which in that respect leaves little to be desired.

For more infusible materials, obstacles are presented which it is the object of the furnace about to be described to overcome. This is done by forcing the ore or other material into the fusion zone by mechanical means.

The furnace structure comprises a base (1), reducing chamber (2), and shaft (3), the latter for the introduction of the charge and the removal of certain of the gases formed in the operation.

The base may be formed of a series of masonry arches supporting the superstructure and enclosing a collecting chamber (15). Within the furnace and above the base are horizontal electrodes (4) of carbon supported by masonry piers (8) and provided with metallic conductors (5 and 6). On either side of each electrode are vertical retaining walls, and near the upper portion is a charging aperture (9) provided with a suitable closure. In the upper portion, and supported in part by these walls, is a hood or bell (10), flaring outward and downward, and serving for the collection and withdrawal of some of the gaseous products of the reaction. This hood may be constructed of iron or steel for moderate temperature work, or suitable refractory material for operations demanding higher tempera-

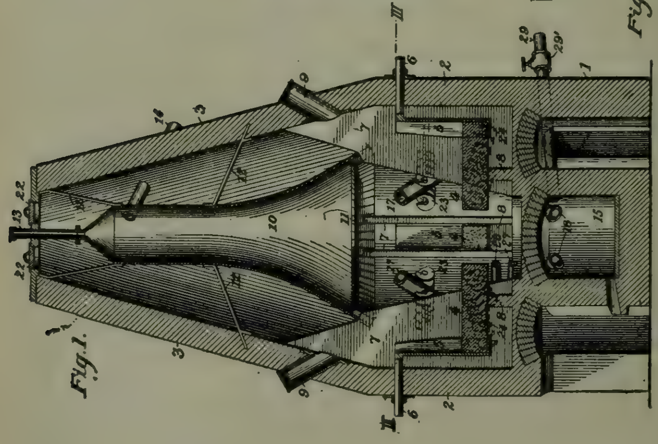

Fig. 1.

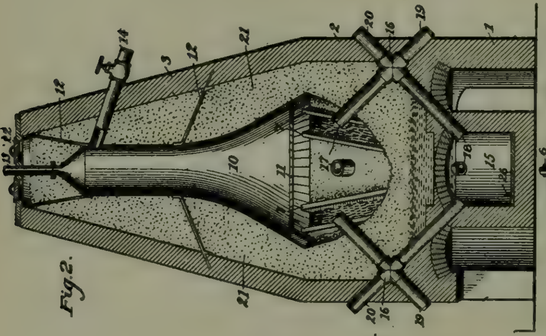

Fig. 2.

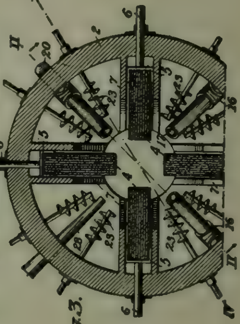

Fig. 3.

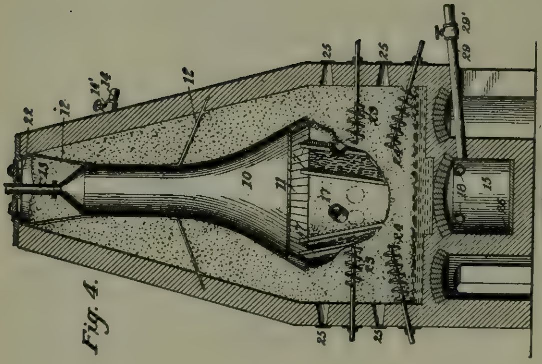

Fig. 4.

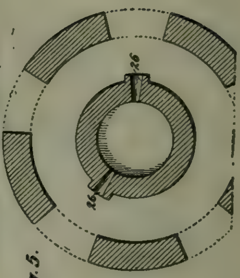

Fig. 5.

tures, or exposed metal portions may be protected with refractory material. (14) represents a pipe for the removal of the lighter gases, such as carbonous oxide (CO).

Within the base of the furnace is the chamber (15) referred to before, which serves for the collection of the volatile metal portions resulting from the reaction. This chamber connects with the furnace proper by means of the conduits (16), which may be made of fire-clay tubes or graphitic carbon, or may be built within the masonry of the furnace. These conduits are provided with legs (17) extending into the interior of the furnace at a point somewhat above the electrodes (or so they will not be covered with the charge passing through the furnace) and with legs (18) extending into the collecting chamber. Legs 19 and 20, in prolongation of legs 17 and 18, pass through the wall of the furnace, and are provided with suitable closures. These extensions afford opportunity for inspection and cleaning of the conduits. In some cases it may be desirable to withdraw some of furnace products through the legs 19.

Adjacent to these conduits, and preferably arranged on two or more levels of the furnace, are a plurality of screws or equivalent mechanical devices (23 and 24), constructed and arranged to continuously, or from time to time, force portions of the furnace charge into the reaction zone. As best shown in Fig. 3, a plurality of these screws are arranged radially around the periphery of the furnace, and in operation serve to force the material into the field of reaction between the electrodes. As shown in Fig. 4, the same screws are mounted in two or more superposed rows, the screws (23) in the upper row being bladed at their inner ends only, while the screws (24) of the lower row are bladed from their inner ends nearly or quite to the furnace walls, and inclined upwardly towards the reaction zone. The purpose and effect of this construction is to ensure that portions of the charge which descend along the periphery of the furnace, past the screws 23, shall be conveyed by the screws 24 to the field of reaction through the surrounding charge.

Ores adapted to being worked in a furnace of this construction are fed into the furnace at the top apertures (22), provided for that purpose. They may be previously mixed with carbon or other reducing material, or, if necessary, with suitable fluxes.

Broken carbons may be fed upon the electrodes as required through openings 9. Several years in the use of broken carbons in the reinforcement of the main carbon electrode has amply demonstrated their great usefulness, both for regulating the current and prolonging the life of the main carbon electrode. For an expenditure of $175 for the main carbons, we have been enabled to produce 2,000,000 pounds of bi-sulphide of carbon in the electric furnace. In much electric furnace work the cost of carbons is a large item in the cost of the finished product, which is here shown to be almost infinitesimal. Certainly not one of the larger of the fixed charges of running a plant.

As the ore is moved forward into the reaction zone, it is replaced by fresh portions from the periphery of the furnace. Any slag or non-volatile reduction products may be drawn off from time to time through the tap holes 27 and 28.

Provision is made for the lighter gases to pass through the hopper 10 and the pipe 14, while the heavier volatile metals may pass more readily through 16 to the receiving chamber 15, entering by the pipes 18, and such gases as are not condensed under such circumstances out through the pipe 29. By controlling the openings 14 and 29, the direction and movement of these gases and vapors may be directed and controlled.

The metal collecting in 15 may be tapped off through the tap holes 26.

This process is designed to minimize the loss of heat from radiation by working ores mechanically and by gravity towards the reaction zone of the furnace, thus securing as far as may be in more difficultly fusible materials the great advantages we have found in this application of readily fusible material, like sulphur, for this purpose in the bi-sulphide of carbon furnace, with which you are already familiar.

DISCUSSION.

MR. C. J. REED: I was going to ask whether the furnace has actually been used for zinc.

MR. E. R. TAYLOR: I have not been able to carry out the operation of the furnace for zinc or anything else on a large scale. About the time that I was undertaking to do that, I had a breakage of the waterwheels which made it impossible at the time, and was led to make several small-scale experiments, which diverted me in a manner from it and, in addition to that, interfered with carrying out the project.

You will recognize that in a furnace of this construction large scale is of the utmost importance. There are certain features that it is absolutely impossible to carry out on a small scale, and I have not yet constructed a furnace of proper scale to develop that feature of the work.

MR. CARL HERING: What is the diameter supposed to be?

MR. TAYLOR: I would think that 10 feet in diameter would be as small as it could be practically worked. Of course, take it in the case of zinc, for example, and provided we knew absolutely, in advance, that it would work, it would be a comparatively small matter to construct a furnace of that kind. It would be a great advantage for zinc, because, as you all know, that work is now done in small retorts, which are very expensive and uneconomical; whereas, to work zinc, for example, in such a large furnace as that, economies would come in that would offset other great expenses in the retort method.

MR. S. A. TUCKER: What material is it that the feed screws shown there are made of? I think there would be chances of melting them down.

MR. TAYLOR: These feed screws were not designed to come into the hotter part of the furnace, and were to stand back in such a position that they would not be subject to the intensest heat; but it was thought to reinforce metal with graphitic carbon (we can easily turn graphitic carbon, as you know, into any form), and it would be comparatively simple to turn a heavy-thread screw in graphite and make them serve that purpose. Moreover, they are not small screws; they would be of some size (and so some strength) that would be put in.

MR. E. A. SPERRY: Would such screws handle solids or ores?

MR. TAYLOR: The ores would be comparatively fine. Of course, you could not put in heavy lumps as big as your fist, or more, and let them come down and drop onto them. It is supposed to be a comparatively fine-powdered ore.

Mr. Sperry: The accumulated ore falls on them both with some pressure?

Mr. Taylor: This is supposed to be full inside of this periphery all the way down, and while the weight of the material would rest on them, there would be no concussion.

Mr. H. H. Emrich: Would it be possible to use this furnace as a simple zinc distiller in place of the retort furnace?

Mr. Taylor: I don't see why it should not be, unless the zinc crust should agglutinate too fast as it comes down. If it would maintain its granular condition, powdering it in the first place and mixing it with special reduction material, as, for example, carbon, it ought to work regularly.

I perceive that I perhaps would have saved time if I had read my paper right through, because it is concisely written. There is provision made for drawing the fused material which is not volatile from the bottom of the heat zone. For example, if we had a mixture of zinc and lead, the zinc would distill and the lead would remain in the bottom of the heat zone and could be tapped off in the way of an ordinary furnace.

Mr. Emrich: You could have a syphon tap in the bottom and have the lead standing at the same depth in the crucible.

Mr. Taylor: Yes. In one of these such provision is made. Here is the tap hole. The provision is made for that tap hole under one of these electrodes; you can tap right directly here.

Mr. Hering: Among other interesting features of that furnace is this one—the heat economy, the heat of the furnace being used to heat the raw material as it comes in. That is right, is it not?

Mr. Taylor: That is the design of the furnace.

Mr. Sperry: I should say that the cooling means between the receiving chamber for the condensed products and the heat zone would be inadequate. You all remember some quite large tests made by Johnson on electric condenser furnaces of this general type, where he was troubled very greatly by explosions of enormous vigor in the receiving chamber. Now, that receiving chamber is so placed that did it explode, of course serious results would follow, and the way that Mr. Johnson succeeded in overcoming that, in a measure, was by introducing between the receiving chamber and the heat zone a very efficient condenser of large surface, so as to get the gases cooled down, and he extracted more product, which does not seem to be provided for quite as much as possibly it might in Mr. Taylor's furnace.

Mr. Taylor: Of course, there are some details that have to be worked out in practice in such a matter. In case of zinc ores, if you make too large a chamber you increase the quantity of the formation of that pulverulent form, or gray deposit of zinc, and it is a long time before you get the full activity of the furnace. These are details that would have to be met as they occurred in practice. There is, however, this to be considered—that the ore is constantly moving by those tubes, and forced on by those screws, so that a change of surface is constantly being brought about which would have a tendency to cool the condensers more than it would if that movement did not take place.

Mr. Sperry: I should think it would warm the tubes, because the ore, coming down from the heated zone, is quite hot before reaching the tubes.

Mr. Taylor: That is true to a very large extent, but the hottest part, of course, of the ores that comes down is near the other part of the furnace, and that which is cooler comes out just above the level of these tubes, so that it is constantly forcing, comparatively, the coolest part of the ore towards these condensing pipes.

I appreciate Mr. Sperry's criticism of this, and I think it is a very important thing to guard against. Perhaps it is not adequately guarded. But it is to be noted that the pulverulent form of zinc will be deposited in any case if the condenser is too large or not sufficiently heated.

A paper read at the Eleventh General Meeting of the American Electrochemical Society, at Philadelphia, Pa., May 4, 1907, President Carl Hering in the chair.

ELECTRIC TUBE FURNACE FOR TEMPERATURE MEASUREMENTS.

By Samuel A. Tucker.

The measurement of the higher temperatures in the electric furnace is one of considerable difficulty, and this is due, for the most part, to the presence of fumes derived from the volatile constituents present, which obscure the readings of the optical pyrometer.

It was with the object of eliminating this trouble that the present furnace was devised.

Other tube furnaces have been described by R. S. Hutton,[1] H. N. Potter,[2] Tucker and Lampen,[3] and A. Lampen,[4] but none of these fulfill the requisite conditions. That of Hutton is very similar to the present form of furnace, but seems to have been used only for relatively low temperatures.

A number of experiments were made with the Lampen furnace, but it was found that with temperatures much above 2000° C. it was impossible to avoid the presence of fumes, which probably come from the granular coke resistor or the charcoal packing used in that furnace.

Fig. 1 shows a side elevation of the furnace, and Fig. 2 an end elevation, showing sections at aa and bb.

It will be seen that the current passes through the carbon tube to be heated, so that the nature of this material is of great importance. It must be pure, so that no volatile constituents will be derived from it on heating, and it must have an appreciable electrical resistance in order to make use of a tube of convenient size. After numerous experiments with Acheson graphite tubes, this material was abandoned, as its low resistance made a very thin tube necessary, and even then to heat it properly required the use of excessively heavy currents. Otherwise this material would be admirable for the tube on account of its purity and ease of machining.

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[1] Electrochem. and Met. III, 455.
[2] U. S. Patents, Nos. 715505 to 715508.
[3] Jour. Am. Chem. Soc., XXIII, 853.
[4] Jour. Am. Chem. Soc., XXIII, 846.

Agglomerated carbon tubes are now made by the National Carbon Co., of Cleveland, and they were found to meet the requirements. The only change in the dimensions made was in turning off a portion in the middle for a distance of about 9 cm., so that the heat is concentrated at this portion of the tube.

What is more difficult to get is a proper material to surround the tube. Such a material should fulfill the following conditions:

(1) Be refractory enough to withstand the high temperature necessary.

(2) Be free from impurities, so that no fumes will be evolved on heating.

(3) Possess high electrical resistance.

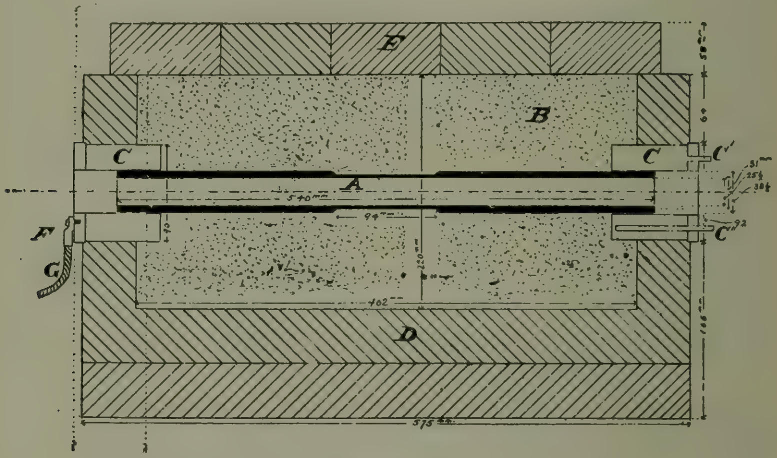

FIG. 1.

Some form of carbon is the only substance which will stand the high temperature, and experiments were made with charcoal, carbonized cotton, and petroleum coke. It was found that charcoal would give fumes at high temperatures, that carbonized cotton (kindly furnished by Westinghouse Co., through Mr. Potter) was an excellent material, but that its tendency to take fire in the presence of very little air made it somewhat inconvenient to handle, and that petroleum coke was the most practical. The latter is a very pure form of carbon, and is a relatively poor conductor of electricity, and although there is some loss of both heat and electrical energy, it does not seem to be excessive.

Two methods were used to unite the carbon tube A to the water-cooled brass holders C. The ends of the tube were copper-plated and then soft-soldered into the holders, or what appears to be equally good is to pack thin-sheet copper or gauze between the tube and the holder. The use of solder means dismantling the furnace pretty well when it becomes necessary to put in a new tube, but the soldered joint makes a very sure electrical connection.

The water-cooled holders are of brass, the joints of which are soldered. The end plate of these holders is made heavy to admit of fastening the lugs F by the machine screws. It would be better to braze the joints of this holder, which would make it possible to soft-solder in the coppered ends of the carbon tube with ease, so that there would be no danger of starting a leak in the holder.

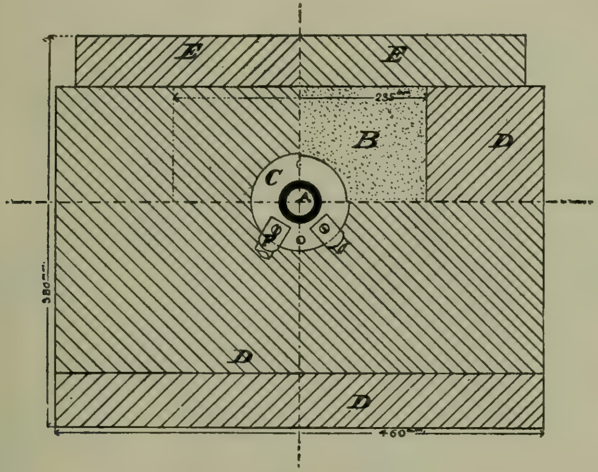

FIG. 2.

From the drawing it will be seen that the carbon tube has a total length of 540 mm., an outside diameter of 38.5 mm., except for the middle portion, where it is reduced to 31 mm., the inside diameter being 25 mm.

The fire-brick enclosure is 575 mm. by 380 mm., the opening 462 mm. long by 235 mm. wide. This opening is filled with petroleum coke B.

The furnace is covered with carbon or other refractory bricks, E. Water is circulated through the holders C by the inlet C″ and outlet C′.

For temperature measurements it is only necessary to place in the middle portion of the tube a small graphite boat, with a disk at one end to fit the internal diameter of the tube. The boat will be raised to the temperature of the portion of the tube in which it is placed, and its temperature is taken with the optical pyrometer sighted through the end of the tube.

For the determination of the melting points of minerals, refractory materials, etc., the disk has a small hole bored in it, which is covered by the material to be melted. A second observer can then look at the disk through a red glass, and as soon as the hole appears in the disk the temperature is taken. With the pyrometer at one end and the observer at the other end of the tube, a close determination of the melting point can be made.

The following tables give the temperatures obtainable with this furnace. The current used was alternating:

TABLE I.—(Low Temperatures)

Minutes	Amperes	Volts	Temperatures
4	330	6-8	1200°C.
5	340	. .	1248
6	460	. .	. .
7	500	. .	1500
9	520	. .	1652
10	550	. .	1688
11	600	15	1860
15	680	. .	2088
16½	700	. .	2120

TABLE II.—(High Temperatures)

Minutes	Amperes	Volts	Temperatures
7	600	15	1752°C.
8	750	. .	2194
8½	760	. .	2284
9½	760	. .	2400
11	760	. .	2660
12	765	. .	2788
14	850	. .	2952

Electrochemical Laboratory,
Columbia University.

A paper read at the Eleventh General Meeting of the American Electrochemical Society, at Philadelphia, Pa., May 4, 1907, President Carl Hering in the chair.

A GRANULAR CARBON RESISTANCE FURNACE.

By Samuel A. Tucker.

A furnace using a resistor of granular carbon has been found particularly serviceable in laboratory work, although of very simple construction.

Oliver P. Watts[1] has given a description of a furnace somewhat similar to the one here presented, but it seems to have had but one application, *i. e.*, to the melting of iron, whereas the uses of such a furnace are numerous and constitute a very efficient method of bringing about thermic reactions.

The dimensions of such a furnace will naturally vary with the source of power available, but the following description applies to a furnace for a maximum capacity of 30 to 35 kilowatts.

As shown in Figs. 1 and 2, the granular resistor, A, is retained by the magnesia bricks, F, at the sides and bottom. The electrodes, C, of Acheson graphite, are luted in at E by a cement composed of equal parts of fire clay and siloxicon. The fireclay brick work, D, is laid in the same cement, all joints being closed tight. The resistor, A, is of crushed gas coke, and no particular care is used in grading it to a certain size; it will probably average 20 mesh, and the finer sizes are to be avoided, as it will cause blowing, which scatters the coke by the gas pressure formed.

The crucible, B, also of graphite, may vary in size, but that shown in the figure has been found to give satisfaction, although a smaller size turned from the regular 2-inch electrodes answers in many cases.

A great difference has been found in using coke for the resistor which has been previously used for resistor purposes, as compared with fresh coke as it comes from the gas retorts. If new coke is used, it will take a much higher voltage to start

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[1] Electrochemical and Met. Industry, IV, 273.

the run, and great care must be taken not to get too great a gas evolution during the time that the volatile matter in the coke is being eliminated; otherwise, the same blowing will take place, causing the general derangement of the furnace. With old coke, it is easy to start the run, and there is little chance of blowing; the crucible can therefore be heated to a high temperature in a very short time. Indeed, with a furnace of the dimensions shown, we have been able to reduce any oxide which can be reduced in the arc, with the great advantage that the temperature is more easily regulated and a more uniform product obtained.

The usual difficulty of increasing the carbon contents, due to the retaining vessel being of that material, is naturally present in this furnace, as in all others using carbon. It is, however, possible to substitute a magnesia crucible for the graphite if the required temperature is not above the melting point of magnesia.

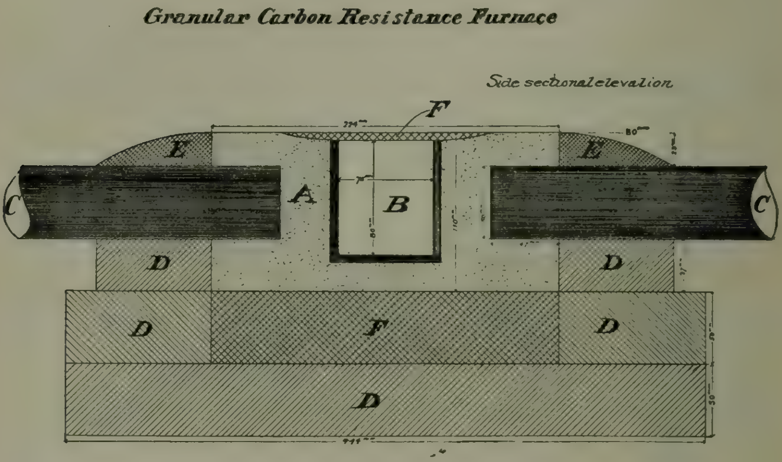


FIG. 1.

Alternating current is most suitable for operating this type of furnace, as perfect control may be obtained by varying the voltage by means of the field of the alternator or by means of an auto-transformer. With direct currents, the rheostat would have to take very heavy currents, and there would be great loss of power. With a furnace of the size shown, it will be found that the crucible will not be heated evenly, particularly at the start, and this is because there is a concentration of the current density at the points a and a′ (Fig. 3), in fact, these points will probably reach a higher temperature than the other portions of the crucible at all times.

If this proves an objectionable feature, it can be largely overcome by packing charcoal around the crucible at these points, as is indicated in Fig. 4. This is easily done by placing a curved piece of sheet iron at the position b and b′ when filling in the coke; the open space between the crucible wall and the sheet iron is then packed with charcoal, and the sheet iron withdrawn. The charcoal, being practically a non-conductor, causes the current to pass to the sides of the crucible.

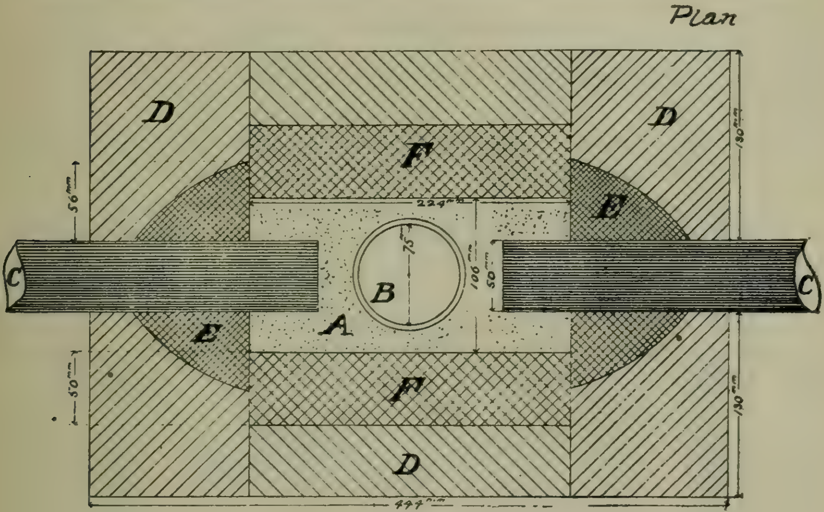


FIG. 2.

Any suitable cover will do to retain the charge in the crucible. These can be easily turned from graphite, and may be fitted with a flange fitting within the crucible, as in Fig. 5, but where elimination of gases is necessary, as in an operation of reduction, a disk of graphite will be found better, as in Fig. 6.

For the treatment of a large quantity of material, a shaft turned from a graphite electrode, fitting within the crucible, as in Fig. 7, is very satisfactory. When melting oxides, such as magnesia, there is a considerable shrinkage, and new material is thus supplied from the shaft to the heated portion of the crucible. This arrangement also acts as a condenser, retaining any volatilized portion. In the case of magnesia this is important, as at ordinary pressures there is a considerable loss of material due to this cause.

It is exceedingly difficult to determine the temperature by the optical pyrometer in this furnace, due to the presence of fumes, which are evolved from the ash in the coke, as well as the heated brick walls.

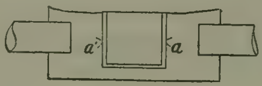


Fig. 3.

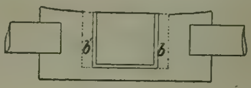


Fig. 4.

Several attempts were made, however, with a graphite tube, the end of which fitted into the crucible, and through which the pyrometer readings were made from the side of the furnace.

The following table gives the results obtained, but the higher readings are evidently obscured by the fumes:

Table I.

Minutes.	Amperes.	Volts.	Temperature.
7	420	28	1520° C.
10	. . .	. . .	1583
13	415	. . .	1600*
14	550	30	. . .
15	. . .	. . .	1640
15½	. . .	. . .	1664
17½	. . .	. . .	1725
19½	. . .	. . .	1812
21½	. . .	. . .	1812
23½	700	42	. . .
25	. . .	. . .	1879
26	. . .	. . .	1980
28	. . .	. . .	2030
30	. . .	. . .	2120
31½	. . .	. . .	2120

* Slight fume.

The probability is that the last readings are much too low. The next run was made with a different resistor, in the attempt to obviate the presence of the fumes, and petroleum coke to which was added a little graphite, for conducting purposes, was substituted for the crushed gas coke.

FIG. 5.

FIG. 6.

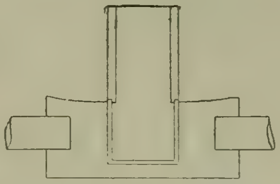


FIG. 7.

TABLE II.

Minutes.	Amperes.	Volts.	Temperature.
3	460	30	1346° C.
5	450	30	1517
7	470	28	1583
9	540	28	1605
12	. .	. . .	1796
13	. . .	. . .	1861
14	. . .	. . .	1879
15	. . .	. . .	1935
17	525	32	1957
19	. . .	. . .	2030
21	.	. . .	2120
23	. . .	. . .	2120
25	. . .	. . .	2120
27	. . .	. .	2120
28	600	38	2156
30	615	33	2280
34	605	33	2280
35	720	35	. . .
36	. . .	. . .	2400*
38	. . .	. . .	2340*
Passed current of hydrogen through the tube.			
7	715	33	2480 2450

* Fumes present.

The dropping temperature in the latter readings indicates the presence of fumes here also, but it shows that with pure materials for the resistor more accurate temperature readings are possible. Both runs would indicate temperatures considerably above those obtained, and the maximum was probably nearer 2700°.

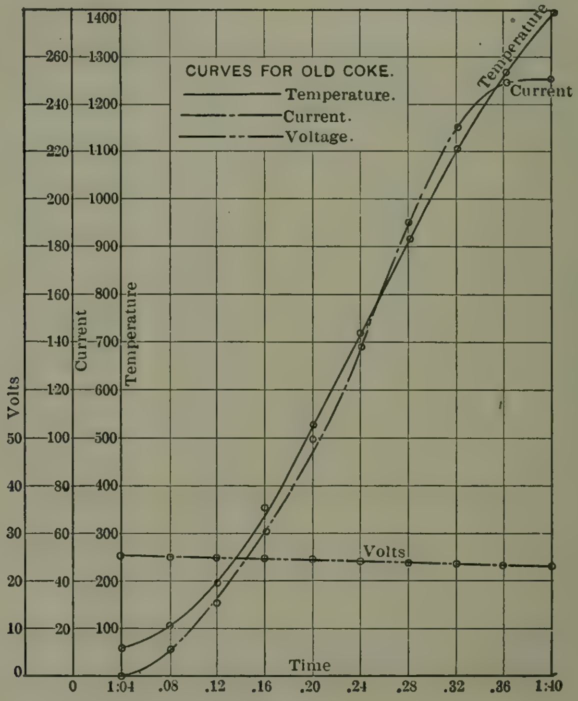
The following tables show the conditions under which reduction is effected:

TABLE III.

Charge—Rutile, 80 parts; Petroleum Coke, 24 parts.

Minutes.	Amperes.	Volts.
5	200	50
7	400	51
8	540	42*
10	600	42
12	670	38
13	670	38
14	710	40
15	700	41
16	700	41
17	800	41
19	820	42
20	800	41
21	810	42

*Strong evolution of gas.



Product gave fine crystals of titanium carbide.

The next run was made with less carbon for reducing purposes.

TABLE IV.

Minutes.	Amperes.	Volts.	Minutes.	Amperes.	Volts.
2	530	44	6	700	46
3	600	52	9	800	52
4	650	50*	11	830	43

***Gas evolved rapidly.**

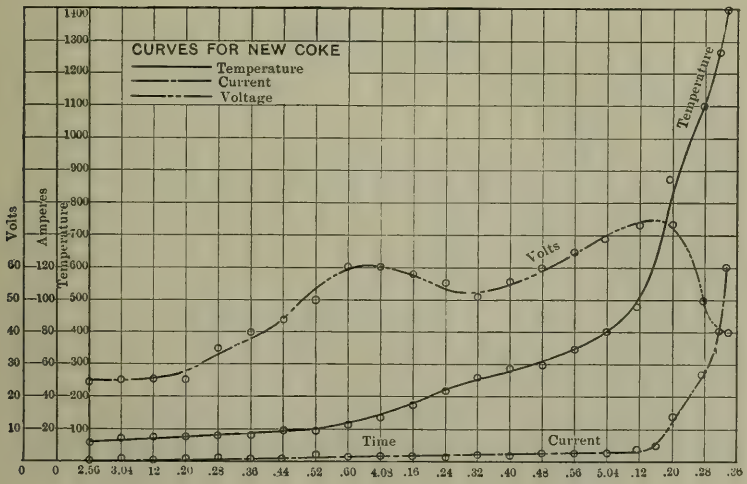
The product obtained was a fine metallic regulus. When pure titanium oxide is used in the proportions of 100 of the oxide to 32 of petroleum coke, a fine product was obtained, using 900 amperes at 38 volts for fifteen minutes.

A run was made on chromium oxide and carbon as follows:

TABLE V.

Charge was 152 parts Chromium oxide ; 32 parts Petroleum coke.

Minutes.	Amperes.	Volts.	Minutes.	Amperes.	Volts.
Start	25	80	14	39	100
7	300	100	17	150	40
10	15	81	22	230	44
11	15	88	26	300	45



The product was in this case good cast chromium and the coke used for the resistor was fresh, which accounts for the irregular current conditions.

It seemed desirable to study the difference in running this type of furnace with new and old coke, and some experiments were undertaken by two of my students, F. C. Loring and V. Skillman, to determine the relation of temperatures obtainable when using the two varieties of coke with the energy impressed.

The results obtained by the use of the optical pyrometer were unsatisfactory, because of the presence of fumes interfering with the pyrometer readings, so that the experiments had to be carried on with an ordinary platinum thermo-couple, which limited the temperatures obtainable to about 1400° C.

The preceding curves are the result of these experiments, and show that the time required to reach the same temperature is very much longer for the new coke than for the old. The energy consumed in either case is about the same as figured from the product of the current and voltage.

Electrochemical Laboratory,
Columbia University.

DISCUSSION.

President Hering: What was the voltage used in the granular furnace?

Prof. Tucker: If you use old coke, the voltage would be pretty low, down to 30 to 40 volts, and the current may reach 700 or 800 amperes or more in a furnace 6 inches long and 4 inches wide, and, of course, that will give you a very high temperature.

President Hering: Another question—how do you fasten those terminals in the carbon rod furnace so as to correct for the expansion of the rod?

Prof. Tucker: We had some trouble with that. The drawing does not show expansion connection. We did have some trouble, and after using the tubes for some little time we found that they bent up in the middle. Unless you go too far, the bend is not very serious. It could be provided for by having a sliding fit on the holders and very flexible connections to them. We did have some such arrangement, but it is not necessary, unless you want to run for a prolonged period of time at a very high temperature.

THE PRESIDENT: In a commercial furnace of that kind does Prof. Tucker consider it absolutely necessary to provide for a flexible terminal for one of the electrodes?

PROF. TUCKER: I think unquestionably it would be necessary on a commercial furnace.

A paper read at the Eleventh General Meeting of the American Electrochemical Society, in Philadelphia, Pa., May 4, 1907; President Carl Hering in the chair.

ON CARBONS FOR ELECTROMETALLURGY.

By F. A. J. FitzGerald and J. Forssell.

Some time ago it was suggested to the National Carbon Co. that a study of the behavior of large carbon electrodes under conditions approximating those found in actual practice would yield useful information for those who employ such articles in electrometallurgical work. While those who have had experience in the use of large electric furnaces are doubtlessly well informed as to the properties of carbon electrodes, there are many who, desiring to use the electric furnace, and having no experience, search for data as to the properties of carbon electrodes, and soon find that these are lacking. The National Carbon Co., falling in with this suggestion, has generously given us the facilities for carrying out the tests which form the subject of this paper, and while the conditions thus obtained are not identical with those found in practice, they are at least an approximation. On account of the method of manufacture, it would be impossible to feel confident in applying the results of tests made on a small carbon to a large one. For example, if we measure the resistance of a carbon 12 inches long and ½ inch in diameter, we cannot calculate its resistivity and confidently apply this to a carbon 8 feet long and having a cross-section of 6 x 6 inches.

The method of experimenting is illustrated in the diagram, Fig. 1, and the key to this diagram is as follows:

A—Carbon graphitized by the Acheson process. Length, 40 inches; cross-section, 4 x 4 inches.

B—Carbon terminal built up of three carbons (amorphous), each carbon having a length of 40 inches, and a cross-section of 3⅛ x 6⅛ inches, consequently the effective cross-section of the terminal is 9¾ x 6 inches.

C—Carbon terminal built up of four carbons (amorphous), each carbon having a length of 72 inches, and a cross-section of 4 x 4 inches; thus the effective cross-section of the terminal is 8 x 8 inches.

D—Amorphous carbon. Length, 40 inches; cross-section, 6 x 6 inches.

E—Amorphous carbon. Length, 93 inches; cross-section, 6 x 6 inches.

F—A carbon similar to C.

G—Amorphous carbon. Length, 73 inches; cross-section, 4 x 4 inches.

H—A carbon similar to A.

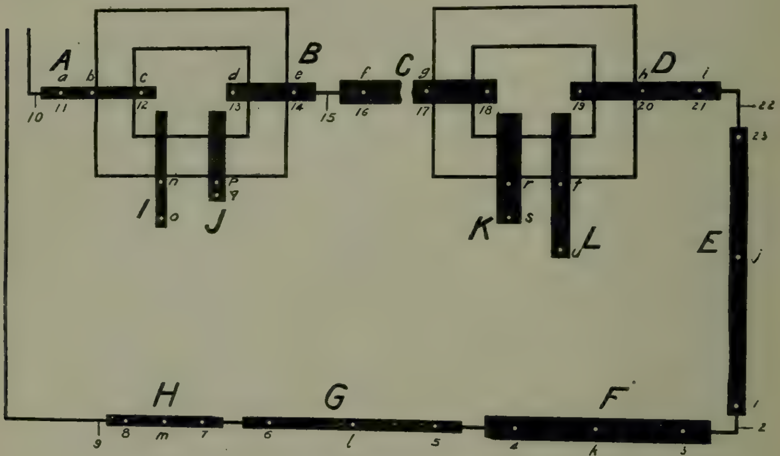


FIG. 1.

The carbons A and B and C and D formed the terminals of two box-like structures built of brick and representing furnaces. The method of constructing these furnaces is shown in Fig. 2, in vertical, longitudinal section, transverse section, and horizontal, longitudinal section. The carbons are in contact with a resistor of granular carbon, and this is surrounded with a mixture of sand and carbon.

In addition to the carbons already described, there are four others, I, J, K, and L, which are not included in the electric circuit. I is a carbon, similar to A, J similar to B, K to C, and L to D.

All the carbons had small holes drilled in them, those marked with numbers (1, 2, 3, etc.) in the diagram being used for making voltmeter connections, while those marked with letters (*a*, *b*, *c*, etc.) were for temperature determinations. At *c* and *d* porcelain tubes passed through the sand and carbon mixture, so that the thermometer or couple could be brought into contact with the carbon inside the furnace.

Besides making measurements of the resistance of the various carbons in the circuit, we also measured the resistance of various types of connection, such as are shown in Fig. 3. A side view and plan of one of these types is shown at *a*. Here the cable is provided with a bronze terminal bolted to two thin copper plates which are clamped to the carbon. The carbons *d* and *e*, shown in side view and plan, are connected with one another by means of a common copper plate clamped between them. In *g* we have another form of terminal, where the carbon is slotted to take an iron clamp provided with threaded bolts which can be screwed down on a copper plate, and this in turn may be connected with the cable carrying the current. In all cases, contact between the copper and the carbon is made by means of graphite. For this purpose, graphite powder should not be used, as it is troublesome to handle. Instead, the graphite obtained by the decomposition of carborundum is used, or that variety of graphite

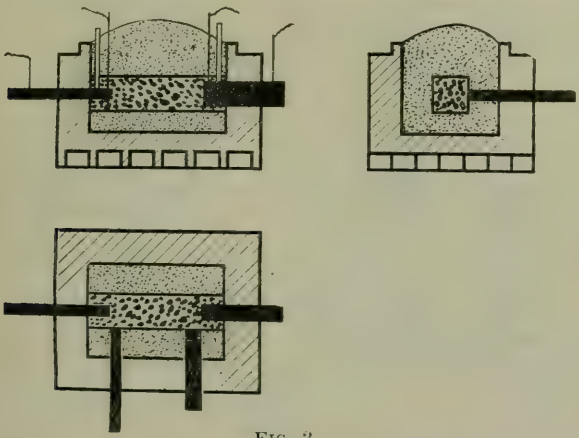


FIG. 2.

known as "Unctuous Acheson graphite" is suitable. Finally, a pure Ceylon graphite may be used, but in this case should be previously treated in the following manner: The graphite is ground down so as to pass through a screen of ⅛-inch mesh, and is then thoroughly moistened with concentrated nitric acid. The mass is then gently heated at first, and finally brought to a dull red heat. This causes the graphite to intumesce, and it may then be used for making connections.

The current supplied to this circuit was single-phase, 60-cycle, with variable voltage. The maximum voltage used was 87, the minimum 66. The maximum kilowatts used were 92. The total time of the experiment was eight hours. During the experiment, readings were taken of the kilowatts and the volts between the various points, 1, 2, 3, etc. Temperature determinations were made at the various points marked *a*, *b*, *c*, etc., on the diagram.[1] Fig. 4 is from a photograph showing the arrangement of the circuit.

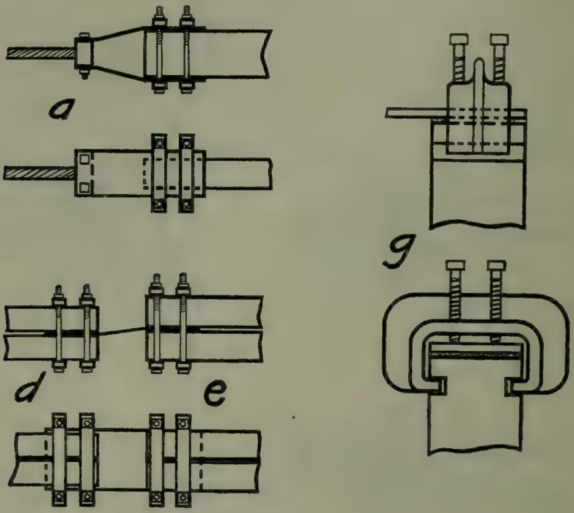


FIG. 3.

At this time we shall not give all the results obtained, as it

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[1] During the experiment which forms the subject of this paper, there was no ammeter in the circuit, so that we could not determine the power factor. We have since repeated the experiment with an ammeter in the circuit and find the value of cos. φ is 1 within the limits of accuracy of the experiment.

would make the paper inordinately long, and, moreover, we have not had time to work out all the results.

Amorphous Carbons.—In all cases, the dimensions of the carbons used in the experiment were carefully determined, and the resistivity calculated from the resistance determinations—that is, the resistance of a cube of the carbon, 1 inch or 1 centimeter on the side, was calculated. The results were as follows:

TABLE I.

Carbon	Resistivity		Temperature Centigrade
	1 in. cube	1 cm. cube	
E	0.00160	0.00406	61°
E	0.00156	0.00396	208°
E	0.00153	0.00389	239°
G	0.00163	0.00414	10°
G	0.00158	0.00401	282°
G	0.00153	0.00389	390°
G	0.00150	0.00381	466°
F*	0.00170	0.00432	10°
F	0.00165	0.00419	126°
D	0.00168	0.00427	——
D	0.00158	0.00401	209°
D	0.00157	0.00399	256°
D	0.00155	0.00494	302°

* The reading of the volts between 3 and 4 showed great irregularity, so that there is some doubt as to the accuracy of these determinations.

Graphitized Carbon.—There were two graphitized carbons in circuit, A and H, but for a reason which will appear later, the determinations made on H are the only ones of value. These are as follows:

TABLE II.

Resistivity of H		Temperature Centigrade
1 in. cube	1 cm. cube	
0.000416	0.001057	10°
0.000387	0.000983	62°
0.000356	0.000904	109°
0.000349	0.000886	——
0.000338	0.000858	185°

TABLE III.

Resistance of Connections.

Carbon	Voltmeter leads	Type of connection	Resistance	
			Per inch²	Per cm.²
H	8- 9	*a*	0.0053	0.0342
G	15-16	*d e*	0.0153	0.0871
E	1- 2	*g*	0.0059	0.0381
E	1- 2	*g*	0.0056	0.0361
E	1- 2	*g*	0.0054	0.0348
E	22-23	*g*	0.0062	0.0400
E	22-23	*g*	0 0063	0.0406

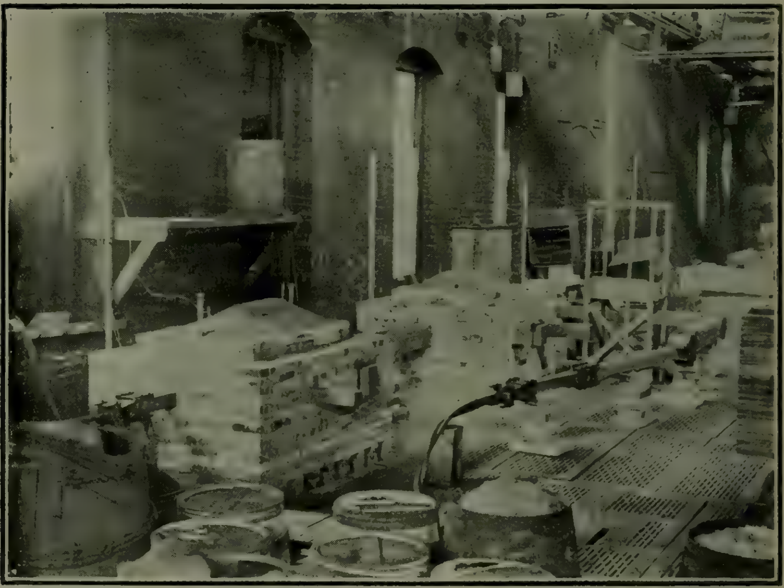

FIG. 4.

Resistance of Carbons in Furnaces.—In the experiment, as originally planned, we expected to get some interesting information as to the resistivity of the carbons at high temperatures from the electrodes A, B, C and D, which were used as furnace terminals, but a curious phenomenon was observed which prevented us from obtaining any useful figures. In every case there was an abnormally large voltage difference between the part of the carbon outside the furnace and the part inside. Consequently, when the resistivity was calculated, it was found to be apparently very high.

Thus the following table shows some of the results obtained:

TABLE IV.

Carbon	Voltmeter leads	Apparent Resistivity	
		1 in. cube	1 cm. cube
A	11-12	0.00303	0.0077
B	23-24	0.00899	0.0228
C	17-18	0.0130	0.0330
D	19-20	0.0126	0.0320

We have not been able to discover the cause of this phenomenon.

Temperatures of Carbons.—The results obtained from the observation on the temperatures of the carbons are very interesting, but examination shows that it will be necessary to make more extended experiments before really useful information is obtained. At the present time, therefore, we can only give some general results.

As might be expected, comparing the maximum temperatures reached by carbons G and H, the latter shows less heating, on account of its lower resistivity.

Each of these carbons had a cross-section of 4 x 4 inches, and therefore the rate of generation of energy in unit length of the carbons was proportional to the resistivities. The maximum temperature attained by G was 472° C., while for H it was 185° C. In the amorphous carbon F, which has 4 times the cross-section of H, the rate of generation of energy per unit length of the carbon is approximately equal to that in H; but since the radiating surface is greater, the rise of temperature is less, and thus we find that the maximum temperature was only 126° C.

In connection with the use of graphitized carbons, it is important to note their high heat conductivity. Thus the maximum temperatures observed in the case of the graphitized carbon A, used in the furnace, and of the graphitized carbon H, which was of the same dimensions as A, were as follows:

Carbon A at *b*	373° C.
Carbon H at *m*	185° C.
Difference	188° C.

On the other hand, if the amorphous carbons C and F are compared we find:

Carbon C at *g*	174° C.
Carbon F at *k*	126° C.
Difference	48° C.

The higher heat conductivity of the graphitized carbons causes a much greater difference in temperature than in the case of the amorphous carbons. This is confirmed by the temperatures observed in the case of the carbons not included in the circuit. The maximum temperatures observed were as follows:

Graphitized	carbon	I at *n*	160° C.
Amorphous	"	J at *p*	52° C.
"	"	K at *r*	74° C.
"	"	L at *t*	67° C.

Thus it is plain that when graphitized carbons are used, the heat losses by conduction are much more serious than in the case of amorphous carbons.

In conclusion, it may be said that this paper is merely intended to give a description of the method of experimenting and a few of the results obtained, but we hope, in the future, to publish further results, and the conclusions to be drawn from them.

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DISCUSSION.

F. A. J. FitzGerald and J. Forssell *(communicated):* Since presenting the paper at the meeting of the American Electrochemical Society, we have made some further experiments, with the object of explaining the phenomenon observed when measuring the voltage drop in that part of the carbons which was inside the furnaces.

To determine if the phenomenon was caused by the use of an alternating current, we applied to the terminals of the circuit a direct current and measured the drop of voltage in the carbons inside the furnace and the amperage of the current. The results obtained corresponded with those found in the case of the alternating current. Therefore, the phenomenon was apparently not due to the use of an alternating current.

There then occurred to us another possible explanation. When a current is passing through an ordinary conductor, such as the carbon electrodes, the equipotential surfaces may be represented by a series of planes cutting the conductor at right angles to the direction of the current. However, when the current passes from the electrode to the granular carbon resistor, surrounded with the mixture of sand and carbon, it is possible that the equipotential surfaces are no longer planes, but may be represented by curved surfaces, and these curved surfaces may be such that they cut the carbon rods which pass through the carbon and sand mixture and the granular carbon from the electrode to the potential lead. If this is so, then in making a determination of the drop of voltage, we would not really determine the volts between the part of the carbon just outside the furnace wall and the end of the carbon inside the furnace, but, instead, the voltage between the former and a point somewhere in the granular carbon resistor. In order to test the adequacy of this explanation, it was only necessary to enclose the carbon rod coming from the end of the carbon inside the furnace in a porcelain tube. When this was done, it was found that the voltage drop was normal, and therefore this represents the true explanation of the phenomenon observed.

MR. SPERRY: Is there any explanation as to why the hotter carbon has the higher resistance? It is supposed to be lower. You do not offer any explanation of the phenomenon you observed. Is this covered in the paper? When carbon increases in temperature, its resistance to flow of current is supposed to be reduced. We now learn that the observations were made when 60-cycle current was flowing in a new furnace and before the same was heated; the drop of potential as the current passes the walls of the furnace indicates them as "green," and therefore electroconductive and acting as a "choke-coil." Thus we find a loss which, in the absence of iron about the aperture through which the carbons pass—which is unexpected and disturbing in its influence—this illustrates an instance where the electrical engineer should co-operate with the metallurgist and chemist for the highest success in the applications of electrical energy to the arts of this class, in which we are interested.

Mr. FitzGerald: You mean that was found in the furnace?

Mr. Sperry: Yes.

Mr. FitzGerald: That phenomenon was observed at the very moment we started, before the carbon had time to get hot. In fact, it was a little less marked when the carbon had become heated.

President Hering: I understand that an alternating current was used in these experiments. In measuring the differences of potential in alternating current circuits, it is important to be sure that there is no induction in the voltmeter leads, because there are cases in which such induction may entirely vitiate the results. I do not refer to self-induction, but to the induction of an e. m. f. in one or both voltmeter leads, due to the fact that one or the other is also cut by the same lines of force which produce the e. m. f. in the main circuit.

Mr. FitzGerald: I do not think that this would explain the results obtained in the present case. The leads from adjacent parts of the carbons used as terminals of the electric furnaces were brought out parallel to one another and close together all the way to the voltmeter. Under these circumstances, a difference in inductive effect in the two circuits would hardly be expected.

President Hering: In measuring the drop of potential in the secondary of an induction furnace like the Colby furnace, which we had the pleasure to inspect yesterday, it seems to me that great care should be taken to avoid this induction in the leads; otherwise, entirely erroneous results might be obtained.

Mr. FitzGerald (replying to Mr. Potter): There were no iron collars around the electrodes going into the furnaces.

Mr. Sperry: You use 60-cycles. Was there an impossibility of an induction being set up in the green walls of the furnace? Were the walls green?

Dr. Forssell: The furnace had just been built, and the walls were green.

A paper read at the Eleventh General Meeting of the American Electrochemical Society, in Philadelphia, Pa., May 3, 1907; Vice-President Richards in the chair.

A PRACTICAL LIMITATION OF RESISTANCE FURNACES; THE "PINCH" PHENOMENON.

BY CARL HERING.

In theory, the electrical resistance furnace is a very simple apparatus; electrical energy is converted into heat in the resistance material with a conversion efficiency of 100 per cent. Theoretically, it might be argued that the only limitations to the temperature are the volatilization of the resistor itself, and in the case of liquid resistors, the inability to get a retaining cell or trough, which does not itself melt. It might also be argued that theoretically any temperature within these limits may readily be obtained by merely increasing the current density to the required amount. Or in other terms, that the temperature increases with the watts per cubic inch in the resistor, and that theoretically, the latter can be increased to any amount without limit by either increasing the energy or diminishing the volume of the resistor.

This amounts to saying that, theoretically, there is no limit to the method of increasing the temperature of a resistance furnace as long as the resistor conducts; hence, all conductors should be capable of being volatilized, just as in the arc furnaces.

Electrical furnaces, therefore, differ in this respect from all combustion furnaces, for in the latter there is a theoretical limit to the temperature, this limit being determined by the initial temperature, the heat of combination of the materials, and the specific heat of the products. To produce more heat, requires that more combustion materials must be added in the same proportion, hence the temperature will not be increased above this maximum; while in the electrical furnace, heat energy may be continued to be added indefinitely to the same limited quantity of material, thereby raising the temperature indefinitely. This is the characteristic difference in the theory of the two kinds of furnaces, and the possibility of higher temperatures is generally the chief reason for the use of the electrical furnace.

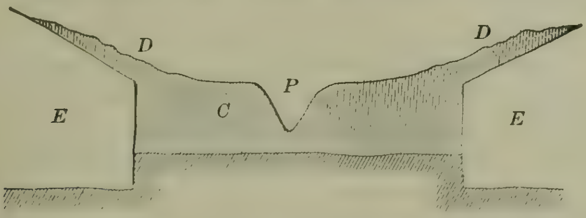
But while such purely theoretical considerations may be of interest and may sometimes be used as a guide, in practice very important limitations and difficulties arise, which may at times make it impossible to obtain the desired temperature, or if not impossible, at least impracticable. It is part of the duty of an engineer who designs such furnaces, to pre-determine, as far as possible, what these practical limits are, so as to avoid building a furnace which cannot possibly produce the desired temperature.

The object of the present paper is to describe a limiting condition sometimes encountered in practice, which appears not to have been known and was very unexpected, and which may at times be serious and perhaps quite insurmountable. It applies to that type of resistance furnace in which the material to be treated forms the resistor, in the form of a column of liquid in a trough, as distinguished from that type in which the resistor is a foreign body like graphite or platinum, which is surrounded or enclosed by the materials to be treated. Of these two classes of furnaces, the latter is by far the simpler in theory, in practice and in operation. Innumerable difficulties encountered in the former are overcome in the latter, and it is probably a good rule to use the latter whenever possible in preference to the former.

As the reason for using an electrical furnace instead of a combustion furnace is generally the high temperature it produces, the conditions encountered in practice which limit the temperature may become very important. In the present paper, the term, limitation, will therefore be used to refer to those conditions which limit the temperature.

It is well known that if a wire be connected between the two poles of a dynamo, it will be heated to a certain temperature. Now, if it be made shorter and shorter, and at the same time smaller and smaller in cross-section, so as to have the same resistance, it will become hotter and hotter, although the current and voltage, and therefore the watts, are the same. In other words, the watts per cubic inch are thereby increased. It might, therefore, be argued that by simply increasing the watts per cubic inch in a furnace, any desired high temperature may be reached, up to that of volatilization, which means the destruction of the resistor.

This, however, is not the case. A limit may be reached which is far below this temperature, due to a curious and surprising phenomenon, which the writer has observed and which he has termed the "pinch phenomenon." This limit may at times be a very serious one, as it is sure to exist, and may sometimes limit the temperature to such a low value as to entirely defeat the object of the furnace. This phenomenon has apparently never been mentioned or described in the leading treatises and, therefore, does not seem to be generally known, and as it may at times be a very serious limitation to the possible temperature in some electric furnaces of this class, it was thought that a description of it and its effect on their operation, may be of interest to furnace designers. Theoretically, this curious phenomenon is also of considerable interest. Dr. E. F. Northrup, of Philadelphia, to whom the author described this phenomenon some months ago, took a great interest in it, and made a very thorough and able study of it, both from the mathematical and physical, as also from the experimental standpoint, including also the quantitative relations. His very interesting paper was read before the Physical Society on March 2d.*



The phenomenon is as follows. When the current density in a liquid conductor in an open channel is increased sufficiently, the conductor will be found to contract in cross-section with considerable force, especially at a place where there is some slight obstruction in the channel, or where, for any other reason, the cross-section is less than the average. This contraction resembles the depression in plastic material that has been pinched between the fingers; as the column of liquid looks as though it were being pinched by some mysterious and invisible force, the writer termed it the "pinch phenomenon," for want of a better name.

In the adjoining figure, *E E* are the cold electrodes of such a furnace; *C* is the column of liquid conductor, which acts as the resistor, and *P* is one of these pinched contractions. The liquid on

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* *Physical Review*, Vol. XXIV, No. 6, June, 1907.

both sides of the contraction slopes like the letter V, with inclinations of 45 degrees and over. The liquid will stay in this position, thus forming a stable state. The inclined surfaces of the liquid, though smooth, showed signs of great internal agitation, as though the liquid was continually running down hill, but was being as rapidly forced up hill again. It was a somewhat curious and interesting sight to see the surface of a liquid sloping at a steep angle and yet be in a stable state. The first impression was that a large leak had suddenly formed, and that the molten metal was rapidly flowing down and out through it; but it was soon found that the condition was a stable one.

When, under these circumstances, the current density is still further increased, this V-shaped depression becomes deeper and deeper until it finally reaches the bottom of the channel; this, of course, breaks the circuit and the liquids then immediately flow together, only to be instantly parted again, thus forming a violent automatic interruptor of the current, accompanied by a sputtering of the metal, loud crackling sounds, and, incidentally, by the great disgust of the man who is running the furnace, as it means that the limit has been exceeded, and if the circuit is not opened at once at the switch, to allow the parted liquids to flow together again to their normal level, there is a strong likelihood that the reduction of the current will cause the core to freeze in this parted condition, which gives rise to serious difficulties in mending the break so that it will carry current again.

If there is any dirt, infusible material or pasty, poorly-conducting slag floating on the surface of the liquid, it will naturally fall into this cavity, and as the conductor in the narrow neck is apt to volatilize, owing to the high current density, while the rest of it is apt to freeze, owing to the reduction of the current, the result is that a complete break is apt to form, through which it may be very difficult and sometimes impossible to start the current again, thus requiring a dismantling and reconstruction of the furnace. It is obvious that this phenomeon places a limit to the current which can be passed through a liquid resistor of given cross-section, thereby limiting the temperature which can be obtained. This limit may be far below that desired, thus completely defeating the purpose of the furnace. It, therefore, is an important factor to be taken into consideration by the designers of this class of furnace. What the limit of temperature will be, will depend, of course, on the particular circumstances; it is evidently not possible to give any fixed rule. It may, perhaps, be subject to calculation, but this is doubtful, as this local pinching seems to be originally induced by some obstacle or contraction in the channel, which, being generally accidental, is not within the reach of mathematics.

It is certain, however, that this tendency to pinching and consequent parting, exists and must be guarded against. If, for instance, a portion of the channel is made smaller than the rest, for the purpose of increasing the temperature locally, great danger exists that this phenomenon will defeat that purpose, and it should first be determined by experiment, whether it will take place, before dependence is placed on the operation of such a design. Under some conditions this temperature limit will be quite low; with mercury, for instance, this pinch phenomenon will take place under favorable conditions before the temperature has risen appreciably.

One of the experiments made by Dr. Northrup, at the writer's suggestion, has shown that if the channel is quite uniform, the contraction in cross-section will also be uniform over its whole length, that is, the level of the liquid will lower uniformly, and, therefore, the danger of parting will not be so great. This explains the observation made by the writer that in a furnace of this type, the liquid conductor kept creeping up on top of the cold electrodes, as at *D D* in the illustration, piling itself up in large quantities, and solidifying after it got there. Fresh material had to be added for some time to keep up the level, until the stable conditions were finally reached. This stable condition is different for each current.

The question naturally arises, how can this pinch phenomenon be avoided. As the forces which cause it, namely, radial pressures toward the central axis, are bound to exist, the only way seems to be to render them as harmless as possible, instead of trying to resist them. To do this, the channel should be made as perfectly uniform as possible and kept free from obstructions. A very liquid flux should be used, if possible, to dissolve any solid foreign particles and to float or wash them away. The cold electrodes should have vertical faces where they are in contact with the liquid resistor, so as to obstruct as much as possible the piling up of the liquid conductor at those places. When the current is stopped, the level of the liquid will become horizontal again, and will, therefore, rise, hence an additional range of regulation must be provided for starting up again with an enlarged cross-section. But, even with all these precautions, an increase of current density will lower the level until at some weak point a rupture will be likely to take place.

Another precaution is to make the channel as deep as possible, and, therefore, narrow in width. The writer noticed, and Dr. Northrup has since confirmed it by experiment, that the force which causes this pinching does not act to produce an unstable equilibrium; the contracting force reaches a stable state when it is balanced by the hydrostatic pressure of the liquid. Hence, by making the channel deep, the tendency to a complete break is reduced. This, however, necessitates making the channel narrow, thereby increasing greatly the tendency to develop a weak spot due to some obstruction or contraction. It also greatly increases the loss of heat through the walls of the furnace. Hence, both depth and width should be made large, which means short channels, low voltages, enormous currents, or else a large capacity of the furnace. In other words, the danger from this source is greatly increased as the furnace becomes smaller in capacity. Some idea of the strength of this contracting force may be had from a case in the writer's experience, in which the V-shaped depression extended down as much as six inches through molten iron to the bottom of the channel, causing a complete rupture, followed by freezing, which necessitated the dismantling of the furnace.

Another good rule, is the brief and well-known one, "don't;" that is, do not use liquid resistors if the conditions permit using a solid one, which heats the materials by contact. There are other reasons, also, for this conclusion.

Another moral to be drawn from this is, do not rely too much on theory; there may be some things still unknown to theory, as it was in this case.

Those interested in this phenomenon from a physical standpoint, are referred to Dr. Northrup's very interesting paper, mentioned above. He therein demonstrates, mathematically, the correctness of the writer's first assertion, namely, that the contracting force was due to the encircling lines of force, and that its effect was, in some, though not in all, respects like that of stretched elastic bands, tending to compress the conductor radially toward the center. He furthermore found that this compression produced a pressure at the center, causing the material there to be forced out at both ends along the central axis, somewhat like when a rubber tube, filled with liquid, is squeezed or pinched with the hand, which will tend to force the liquid out at both ends. With a vertical column of mercury, he has succeeded in thus producing a small fountain of mercury issuing from the center of a large conductor; and by letting this mercury flow back near the outside of the conductor, the fountain plays continuously; thus he produced continuous motion by merely passing a current through one conductor, without magnets, commutators, brushes, bearings, etc., presumably the first time such motion was ever produced. As was originally observed by the writer, the phenomenon is independent of the direction of the current, hence takes place with either direct or alternating currents.

The action might be explained, as Dr. Northrup suggested, according to the principle that currents flowing in a like direction attract each other. Hence, all the linear current elements in a conductor should be attracted to its center, causing a contraction. This does not, however, explain why these current elements should drag the material of the conductor with them; why does not the current simply become denser at the center? An electrical current passing across a running stream does not seem to be carried down with the stream as though it were inseparable from the water, but it always seems to take the shorter path across it; then why should the electric current, when in motion, drag the conductor with it as though it were inseparable from it? Yet it does do so in some cases, as in a unipolar disk motor, and one is therefore led to conclude that this matter has not yet been clearly explained by physicists.

The writer's belief is that his original suggested explanation is more satisfactory, namely, that this pinch phenomenon is due to some action of the ever-present encircling magnetic lines of force, which are all under tension like stretched rubber bands, and therefore exert a radial pressure on the material which carries the current. Dr. Northrup's mathematical investigations confirm this suggested explanation, in so far that he has shown that the contracted conductor has many more lines of force encircling it on the outside, than the original had, when both carry the same current; he shows that many additional lines of force are created by this contraction, and their radial pressures, due to their tension, have therefore been added to that of the others, which were there before; this would explain the increased pressure on the contracted conductor.

The old proverb about the "ill wind" applies here, too, for, although this phenomenon is a serious obstacle in electric furnaces having liquid resistors, it at once suggested to Dr. Northrup an application to simple forms of measuring instruments like those of the indicating and integrating types, that measure direct and alternating currents equally well, and it may raise in the mind of the inventor new visions of the possibilities of the long-looked-for commutatorless direct current dynamo and motor, or self-starting single-phase, alternating current motor.

An analysis of this phenomenon leads to many interesting deductions, which, however, are not in place in a paper on furnaces. One of these is that Ohm's law may perhaps not be strictly true for high current densities. Another is that the action of fuses and of the Caldwell interruptor may be due, in part, at least, to this phenomenon. Perhaps the action of the speaking arc is due to this phenomenon, as was suggested by Dr. Northrup.

This phenomenon should be clearly distinguished from the well-known and entirely different one, according to which a flexible circuit tends to enclose the largest possible area, and, therefore, tries to enlarge itself into a circle. The latter has been observed in induction furnaces, in which, it seems, the molten iron in the circular trough sometimes acts as though it were under the influence of a strong centrifugal force, and to such an extent that the bottom of the trough can be seen.

DISCUSSION.

Mr. C. J. Reed: About twelve years ago I noticed this phenomenon, in connection with Mr. Winand and Mr. Bilberg. We had occasion to use a rubber trough, ½ inch wide and 1½ inches deep, filled with mercury, as a temporary switch, and made connection by inserting copper rods. We attempted to pass about 1,000 amperes through, and did not succeed. The mercury would break almost instantly in the middle, then form an arc, and then come together again. This was rapidly repeated, and the mercury was volatilized and thrown out of the trough. We also found that there was a peculiar vortex formed when two copper conductors were placed in a dish of mercury with a heavy current; a funnel-shaped vortex was formed on the surface of the mercury which remained permanent and assumed a certain particular form of cone when the copper conductors had a certain angle; changing that angle would change the form of the vortex.

MR. H. N. POTTER: This phenomenon is one of great interest, and I would like to know where the pinch would occur in an induction furnace where there are no electrodes?

PRESIDENT HERING: When the core is of absolutely uniform cross-section, the pinch is uniform all over, and it will therefore not be likely to occur in any one place; but if the cross-section is diminished in any one spot, the pinch will take place there. It starts where there is a contraction of the column of liquid, due, say, to some obstruction or some dirt or to some difference in level, and it will continue up to a certain point. It is a stable phenomenon, however; the contraction will continue to a certain point and will stop there; it will not get worse and worse, unless you increase the current; for every current, there is a certain level, at which it will stay. I might add that the explanation of the phenomenon, as Dr. Northrup has demonstrated, is this: We all know that like currents attract; we can assume the conductor to be made up of a whole lot of filaments of like currents; they will attract each other with considerable force, resulting in the contraction of the whole conductor.

MR. POTTER: Can the pinch be caused to move by a superimposed magnetic field?

MR. HERING: I intended trying this, but have not yet done so. I believe, however, that the pinch could be made to move by a superimposed field. The pinching which I observed was due entirely to the magnetic field encircling the conductor, and generated by the current itself. If to this field there is added another one, I see no reason why it should not add to the pinching effect.

A paper read at a meeting of the New York Section of the American Electrochemical Society, in New York, February 26, 1907; Chairman S. A. Tucker presiding.

POWER COSTS.

BY CHARLES E. LUCKE.

Practically all of the modern industries use power in one form or another, more or less largely, so that as a consequence the cost of production contains as one of its elements the cost of power used. Some of the industries are absolutely dependent for their existence upon the possibility of obtaining power cheap enough to enable the product to compete with something else, which may possibly be a natural product (either the same or a substitute). This is the case in most of the electrochemical industries. In other industries the cost of power is a more or less important factor, depending upon the nature of the case. This being the fact, the economy of power production as a problem, while it is to be neglected by none, requires more close and detailed study by those engaged in the industries, which are either absolutely depending upon low power costs for their existence or in those in which cost of power is a large fraction of the total expense.

No matter how important or unimportant the cost of power may seem to the manager of the particular industry in question, true economy demands that it be produced at the lowest possible cost, and a power plant may be considered by itself a factory for the production of power, complete in itself, whether that power be used for one purpose or another. Considering the power plant as a factory, it should be built and maintained to make money, and it will make the most money when it produces power in the most available form for the least possible cost. No power plant should be built to demonstrate any beautiful theory, whether of thermo-dynamics, hydraulics or any of the other applied sciences, and its existence in the form which it may take is justified only on the basis of dollars and cents.

The cost of producing power has been made the subject of numerous articles and official, unofficial and semi-official reports, by individuals or corporations manufacturing power or by individuals or corporations building power plant apparatus. There is in existence, as a consequence, a large mass of figures, representing power costs coming from the builders of plants or from the owners of plants; coming possibly from Government, Municipal, or State reports; coming from any of the foreign countries or from our own country; coming from large plants and small plants, from plants generating power from waterfalls, coal, oil or gas, by steam engines or gas engines, all of various types and form with an infinite variety of combination of the main units and auxiliaries. When it is considered that the motive for publishing these figures may be widely different, in one case to promote the sale of certain pieces of apparatus where the figures are probably too low, in another case to mislead governments contemplating municipal ownership, by giving figures too high, and when in addition to the motive it is rememberel that the apparatus for generating the power to-day is most complex, both with respect to details and systems, and that every variation involves a necessary change of power cost, and when in addition to all this it is remembered how geographical location may enter as a factor, supplying one portion of the country with natural gas, another with cheap coal and another with oil, it will be readily understood that these figures in existence for power costs are of doubtful value.

A further element which enters into the comparison of power costs, as published or obtained from individuals, is the method of accounting employed, which determines to what account each expense incurred shall be charged, and which of the separate accounts kept, properly belongs to the cost of power, either wholly or in part, and if in part, what part? It will be found that the builder of a gasoline engine will speak about power costs and give figures which may on examination prove to be nothing more than the cost of fuel per horse-power hour, when the engine is new and run on its best load, and when the cost of fuel per gallon is some definite figure. The superintendent of motive power of a large railway corporation may report to the board of directors the cost of power, involving all the possible and proper charges, both fixed and operating, for a large plant. The comparison of these net figures with the figures determined as above gives absolutely no information unless each is qualified by showing what elements of expense have been introduced into the power cost, and what part of the expenses that were incurred directly or indirectly were charged to the account. The determination of power costs, then, is not only a question of geographical location, a question of the generating system, a question of the size of the apparatus, a question of the perfection of its design, a question of the load condition, but it is also a question of accounting, and the engineer engaged upon a question of this sort must not only be an engineer but something of a financier and an accountant.

Not many years ago practically all the power used was generated in steam plants, with the exception of a few small gasoline and gas engines, rather unimportant as power producers, and a few isolated water wheels. At that time it was thought that the question of power production had finally become standardized, and that while waterfalls near where power was wanted could be profitably used, everywhere else steam had to be used, either condensing or non-condensing, with any of the various boilers and auxiliaries, but always with the reciprocating steam engine. The design of these stations tended toward a certain uniformity of arrangement that was the evidence of standardization. At the present time, because of a rapid development of perhaps ten years or possibly less, the engineer, whose problem is power production for a certain industry or for itself, is face to face with a variety of systems, each as complicated in its main units and auxiliary apparatus to be used as was the single system, which was the well-known and only standard not so long ago. To-day the question must be gone into: first, on the selection of a system by considering the possible source of energy and the possibilities of power transmission. The development of electrical appliances and knowledge has made possible long-distance transmission, so that the waterfall has practically been brought to any point within a radius of perhaps 150 miles or more from its actual location. In the same way the natural gas field has been brought to the city or the town by pumping by means of gas engine driven compressors. The gas producer has been developed and the large gas engine, so that not only can a gas producer operate a gas engine to-day wherever suitable coal can be bought, but the gas producer can be set down at the coal mine or other convenient point and power transmitted either electrically or by pumping the producer gas through pipe lines. The gas engine has made possible also the better utilization of blast furnace waste, and we find transmission systems abroad supplying neighboring towns with power from these waste gases over what is needed by the mill itself. The oil engine has been developed and the oil tank and pipe lines are realities. The steam turbine has been developed as a competitor of the reciprocating steam engine. We thus have a great variety of systems each with its characteristics, and each no longer limited so much as before, either by size, service, character or by geographical location because of the development of transmission methods.

Engineers designing new work are face to face with the problem of selecting a system, which is to be determined, in part at least, by the power costs of the various systems now in successful use. There is thus a legitimate demand for information on costs. It is unlikely, because of the rapidity of the developments, that the power plant engineer of to-day will have had personal experience with each system, and the confession on the part of such a designer or projector that he knows nothing of one or the other branches or systems of power production, is no criticism of himself or his ability. It is beyond the range of possibility that more than a very small percentage of all those engaged in this work should have data on all the various subjects necessary. To give figures on power costs for a number of different stations of the same size in similar localities and compare them would border upon the illegitimate from a business standpoint, unless it be done with the consent of all interested parties. To give figures for a number of isolated stations of different kinds and different systems that may have been obtained by me personally, either confidentially or not, would be of little value without a full discussion of all the determining conditions and methods of accounting, which would be absolutely impossible in a paper necessarily limited to the length of this. It would require a large book, and such a book I hope some day to get time to write.

For the purpose of stimulating public discussion of this important subject some figures of comparative values will be given for the different systems under certain assumed conditions. These figures will further serve as a basis for modification, alteration or extension by anyone interested in the discussion. Before, however, taking up any figures at all it is well to keep in mind the fact that all of the various systems may not be competitive in some particular case, either by reason of their adaptability to the service, of availability of supply or any one of the thousand other local conditions, all of which will modify any assumed figures.

As there is no standard accounting system in use, like, for example, that worked up by the Street Railway Accountants' Association for Electric Railway Work, although there should be, the following cost division will be used here without specifying the various expense items that should be charged to each. The total cost will be divided into fixed and operating charges.

Fixed.—Interest.
Depreciation.
Insurance.
Taxes.
General office expense.

Material in operating.—
Fuel and water.
Oil, waste, packing and miscellaneous supplies.

Operating.—Labor in operating.
Maintenance and repairs, including labor and material.

POWER COSTS.

The fixed and operating charges are the same in nature for all different power systems, but different in kind in some cases. Interest may be figured at any rate from 3 per cent. to 6 per cent., depending upon a large number of circumstances, which cannot be gone into here, but whether the amount of investment, the interest of which is charged against power cost, will include real estate on which the power plant is built or not, is a question of doubt, and there is still more doubt, or rather lack of agreement, on the question of interest charges on real estate used for the storage of coal, ashes, or, in the case of water power, of land covered by the pipe lines, reservoirs, dams, the property that had to be purchased to permit the rise in level of the natural stream after the dam is built. Not only is the doubt about the interest charges of this kind, but when real estate is in question there rises a possibility of credit item or an appreciation to offset the interest in the nature of what is so often called the "unearned increment." Depreciation as a fixed charge against power cost is an item on which there is practically no agreement except as to the necessity of including it in some form or other.

Depreciation may represent an amount which should be charged against earnings, each year, for the renewal of any part of the plant on the assumption that that part will need renewal. In this sense each part of the plant is given an assumed life of X years and the first cost of that part divided by X is charged off yearly to a sinking fund, but whether this sinking fund, thus created, should be considered as earning anything or not, or whether it should be considered invested at simple or compound interest or not, presents still another doubt. Depreciation may also be considered to mean the difference between the first cost of the plant, or any part of it, and what it would bring in the open market second-hand or as scrap, or, if real estate, at public auction. Thus depreciation of the present value of the plant or any part of it is naturally a very uncertain thing and open to manipulation by unscrupulous persons, who desire to make the plant appear better or worse than it really is, as well as being open to honest misunderstanding based upon difference in judging. The third possible meaning for depreciation is quite different. It is assumed that the plant exists for making money. It, therefore, has a certain earning capacity and is capable of yielding certain profits. So long as it is capable of continuing to earn these profits it may be assumed to have a value equal to what it always had, and, therefore, depreciation is nothing. This depreciation is judged solely from the point of view of the earning power of the invested capital in the particular business in question. This is rather the unusual point of view.

It is certain that if the machinery and equipment of any kind be thoroughly overhauled and repaired that it will be worth more than if it had not been overhauled, and therefore, it would seem that depreciation should have some relation to the item of "repairs and maintenance," which is usually considered an operating charge. This relation is, however, seldom given proper consideration.

The third class of fixed charges common to all systems is the item of insurance and taxes. Insurance itself may cover fire, water, flood, lightning, accident and employers' liability, and is dependent upon the original investment or the amount of liability in question. It may vary from ½ of 1 per cent. to 10 per cent. of the total amount invested, excluding real estate and accident and employer's liability, which, of course, cannot be valuated. Taxes are dependent upon municipal and State regulation, and are so different in different localities that while the item should be charged against power cost in any case, in comparing costs this should be eliminated.

The usual practice in comparing systems involving different charges is to give to each a reasonable value, but the discussion will never settle the question, "What is the reasonable value?" and whether that value should be different for different systems.

Operating costs should, of course, include all labor, including beside that immediately concerned with the running of machinery also an amount for bookkeeping, superintendence and even janitorial. All fuel, all lubricating oil, grease, waste, pipe fittings, fuses and other material used about the plant, either for operation, maintenance or repairs, is properly an operating charge, but so are also smaller items such as expressage, telephone bills, ice water and little things nearly always forgotten or charged to that indefinite account, "general expenses," which means nothing.

In charging these items to operating expenses it is common to simply report for water power, "labor and maintenance," as one item, and "supplies" for the other, giving only two items for operating expenses, while for steam, gas and oil power plants there are four, 1° fuel, 2° operating labor, 3° oil, waste and miscellaneous supplies and 4° maintenance and repairs, including both labor and materials.

Water Power:

Water power generally is the cheapest but is not always necessarily the cheapest. The water itself costs nothing, but it cannot be used as nature provides it. The cost of preparing it for proper use in wheels and of providing for its control will involve a considerable expense, as a rule, and the interest on this expense will correspondingly be the largest charge against power cost, and will, as far as its importance is concerned, be commensurate with the fuel charges in gas engines, steam engines or oil engines. The cost of developing water power depends almost entirely on the local situation, and cannot be reduced to any formula or rule. In the early days of the water power development—say over 1,000 horse-power—only low heads were utilized and the wheels located at the side of the dam, making the total development involve nothing more than a timber and stone dam with a house at one end. As the demand grew for more power from the same stream it was necessary to dig a canal to bring the water around the original power-house to some other house. Thus the expense began to increase from difficulty of bringing the most water to the wheels under the largest heads by long pipe lines or combinations of pipe lines, canals, flumes, tunnels and vertical shafts, so that the cost has materially increased. The simpler development complete cost somewhere about $40.00 per horse-power without electrical equipment. This has now increased so that a minimum of $75.00 per k. w. is considered a very good proposition, while a maximum of $200.00 per k. w. is not by any means prohibitive, including electrical equipment. The mean is somewhere near $100 for very large installations favorably placed like Niagara. Taking these two limits and a gross interest charge of 5 per cent. with an average depreciation of 4 per cent., with insurance and taxes at 1 per cent. there is a total charge of 10 per cent. on the first cost or $7.50 per k. w. year as a low limit, and $20 per k. w. year as a high limit. The operating expenses, labor, oil, waste, repairs, etc., may be expected to cost from $1 to $5 per k. w. year, which places the cost of electric power at the bus bars between the rare low limit of $8.50 per k. w. year and the high limit of $25 per k. w. year for full load, 24-hour power for these rates of charging expenses. Beside the increase in development cost there is another item that sometimes enters, and that is an increase in land expense or land damage, which may be large in settled communities. The increase in cost is not at all due to increase in cost of machinery; this has probably decreased, not only from a better method of manufacture and more competition, but from the use of high heads and better wheels and electric generators.

Just how much can be paid profitably for the development of water power, either now or in the future, will be measured solely by the power cost of that one of the competing systems most available, steam, gas or oil, in the same locality, or if not in the same locality at some point within the limits of electrical transmission. To the cost of generating water power must be added transmission cost, involving fixed charges, on lines, transformers, switchboard and other equipment, together with their maintenance and operating charges. All of these together may add to first cost $30 per k. w. and increase the power cost for a 150-mile transmission $5 per k. w. year.

Oil Power:

Oil engines are not built in large sizes and the variety of engines on the market is small. Therefore, for plants of 1,000 horsepower or more multiple units are necessary, and for a 24-hour output spare units must be installed to insure continuity of the output. The first cost, therefore, must be that for more horsepower than is needed, and just how much more will depend upon the number and size of the units, and will vary from 20 per cent. to 50 per cent. If there are many small units 20 per cent. additional installation will be sufficient. If there are only a few large units, twice as many may be necesasry as is actually called for by the output; in any case the more spare units the less the chance of discontinuity of output and the safer the guarantee of 24-hour power.

To keep a fair proportionality between the computations on the various systems with respect to their size, oil engines of 250 horse-power will be taken for example, coupled to 160 k. w. generators to enable overload capacity to be used. Six such units wil be assumed for a station operating on a 24-hour load, equal to the output of 4 or a rating of 640 k. w. These engines should cost $62.00 per horse-power or $97 per k. w. of generator rating. The oil station including foundations, piping for oil, water and exhaust, electrical equipment, building, crane, etc., should cost about $145 per k. w. on the maximum rating or 150 per cent of this on the 24-hour guaranteed load rating, or $217 per k. w. Taking the fixed charges, including interest, depreciation, insurance, and general office expenses, as equal to

10 per cent. per year on the first cost, the yearly fixed charges become $21.70 per k. w. year. This plant will require continuously one engineer, at about $100 per month, and four engine operators at about $60 per month, which for the above conditions works out 0.15 cents per k. w. hour. The engines should use fuel oil, costing about 2½ cents a gallon, and should consume about 15 gallons per k. w. hour. This gives the operating power costs or the manufacturing power costs as follows:

Fuel oil	0.38	cents per k. w. hour.
Lubricating oil, waste, etc.	0.04	" " " "
Operating labor	0.15	" " " "
Maintenance and repairs	0.08	" " " "
Total	0.65	" " " "

For a year of 8,760 hours this amounts to $56.94 per k. w. year. Adding this operating cost to the fixed yearly charges of $21.70 per k. w. year gives a total power cost of $78.64 per k. w. year.

Any change in the cost of fuel from that assumed will affect the result. Changes in local conditions and price of labor, different grouping of engines to make more or less men necessary, insurance, interest and repairs will all have their affect on this cost. A more economical engine than this one assumed will have the effect of lowering the fuel oil cost, but it will very slightly increase the lubricating oil, especially that used in the cylinders, so that these two would tend to compensate.

STEAM POWER STATIONS.

There is practically no limit to the size of steam-power stations with reciprocating engines, but there is a practicable limit to the size of units, and very large powers are to be obtained by multiplying these units. In order to make a fair comparison, a steam-power station will be assumed of the most economical type, not necessarily the largest size, but involving very close to the largest units. This is what was done with the oil plants, although there the line of separation is not quite so marked as here. As a typical example, assume a 20,000 k. w. 24-hour load. The station to carry this must be, at least, of 30,000 k. w. capacity, which for 5,000 k. w. units calls for four at work all the time; two in reserve with auxiliaries and boilers accordingly. Such a station with all the latest labor-saving devices, with coal at $3.00 per ton, and water at $1.00 per 1,000 cubic feet, will have about the following division of operating power costs:

Coal	64	per cent. of the total.
Water	8	" " " "
Operating labor	12	" " " "
Oil, waste, etc.	4	" " " "
Maintenance and repairs, including both labor and supplies	12	" " " "
Total	100	per cent.

Such a station may be expected to operate year in and year out on about 2½ pounds of coal per k.w. hour, and about 30 pounds of water per k. w., including that for the engines as well as for cleaning, washing, heating, etc. At these rates, with the above division of power costs we have the following:

Coal	0.380	cents per k. w. hour.
Water	0.048	" " " "
Oil, waste, etc.	0.024	" " " "
Operating labor	0.076	" " " "
Maintenance and repairs, including labor and supplies	0.072	" " " "
Total	0.600	" " " "

With this 24-hour load throughout the year of 8,760 hours per year, the cost per k. w. year, excluding fixed charges, will be as follows:

Coal	$ 33.29	per k. w. year.
Water	4.20	" " "
Operating labor	6.66	" " "
Oil, waste, etc.	2.10	" " "
Maintenance and repairs, including labor and supplies	6.31	" " "
Total	$ 52.56	" " "

Such a station as this may be expected to cost, excluding real estate, but including vertical reciprocating engines, boilers, stokers, stacks, condensers, feed water heaters, economizers, boiler feed, hot well and dry vacuum pumps, house service pumps, exciter units, steam, water and exhaust piping, pipe covering and painting, drip return system, lubricating oil system, plumbing, coal and ash handling system, house heating system, elevators, cranes, electric generators, switchboards and wiring, and building complete, from $110 to $150 per k. w. generator rating. Taking interest, depreciation and general office expenses, equivalent to a total of 10 per cent. per year on the first cost, there results fixed charges from $11 to $15 per k. w. year on the expected output rating. For the 24 hours, however, there is provided, in this station, a 50 per cent. reserve on the rating, so that the actual charges will be 150 per cent. of this, or from $16.50 to $22.50 per k. w. year. Adding this to the manufacturing power cost of $52.56 per k. w. year gives as a fair value for the total power cost of such a highly refined, large, steam station $69 per k. w. year to $75 per k. w. year. Of course, changes in the design of the station and local conditions may lower this operating power cost, but not very much. Fixed charges can, as a rule, be reduced only by simple arrangements and cheaper apparatus, which will involve as a consequence less economy and higher operating costs.

A small steam station very much less economical than this will involve power costs much higher than this. The station will be cheaper, but it will burn more coal and require more labor. The power costs, as shown by some of these smaller stations may be over 1 cent, and as high as 5 cents, for very small stations per k. w. hour, which is from two to nine times the operating costs assumed for this large station. The first cost of the equipment may be as low as $75 per k. w., which is approximately half what was assumed for the large, refined station. The results of such a variation will generally be a higher yearly power cost than assuming above for the smaller station.

The use of steam turbines in place of reciprocating engines will have the effect of reducing first cost approximately $10 per k. w., and it will also have the effect of increasing the coal and water costs and decreasing the operating labor costs. The net result will probably not be very different than for the reciprocating engines. If there is to be any change, it will probably be an increase in power cost, rather than a decrease, excepting where real estate is included, and real estate at the same time very expensive. The small space occupied by the turbines will decrease the fixed charges on real estate probably enough to bring the balance of total power cost, in such a station, slightly in favor of turbines.

GAS POWER.

Gas-power stations involving gas engines and producers have not yet been built as large as steam stations, and 1,000 horsepower units may be assumed to be, in connection with 600 k. w. generators, about the largest size units on which there is practical data of long period operation. Taking up for a typical gas station one containing four (4) such units at work and two (2) in reserve, the station would be capable of delivering four times 600, or 2,400 k. w. 24-hour loads every day in the year. The station would, however, have a maximum rating of 3,600 k. w. Such a station would cost approximately $180 per k. w. complete, the engines and producers costing $56.00 per k. w., unset, and the rest of the first cost of the station being divided up between foundations for engines and producers, electrical equipment, gas, water, exhaust, steam and air blast, compressed air piping, coal and ash-handling apparatus, exhaust silencers, gas holder for regulating pressure and controlling producer, air compressor and tank for starting, building, crane, small auxiliary boiler for producer house, and all auxiliaries and incidental apparatus.

As the station output actually counted on is only two-thirds of the maximum rated capacity, the fixed charges must be figured on the basis of 150 per cent. of $180, or $270 per k. w. for first cost. When, as before, the fixed charges, including interest, depreciation, insurance, general office expenses, etc., equal 10 per cent. yearly of the first cost there results a fixed charge yearly of $27 per k. w. year, as against $22.50 maximum for the steam station. This station will be charged nothing for water, because there are no boilers to scale, except the small auxiliary producer boiler, which may be neglected. If, however, water is to be charged in any particular case, it may be figured on 200 pounds, circulating, necessary per k. w. hour for all purposes. The coal consumption will work out, in such a station as this, about 1½ pounds per k. w. hour, the coal being anthracite No. 1 buckwheat, which may be assumed to cost $3.00 per ton. This coal consumption will be practically the same for any size of plant, and it is interesting to compare it with what might be expected in steam plants, which for even the large size assumed of the highest economical type is 2½ pounds per k. w. year, and for smaller steam plants, might easily run up to 3 or 4 pounds per k. w. hour. These coal consumptions are, of course, not the best that can be obtained in any of these plants, but figures that can be depended upon, with the apparatus in ordinary condition in the hands of ordinary operators, the year 'round, and are drawn from actual experience, and not from any particular test with everything in fine condition and correct adjustment.

The coal cost per k. w. hour will be, on the above basis, 22 cents, and the other operating costs can be figured from the following distribution:

Coal	50	per cent. of the total
Operating labor	23	“ “ “ “ “
Oil, waste, etc.	7	“ “ “ “ “
Maintenance and repairs	20	“ “ “ “ “
Total	100	per cent.

This gives for the operating power costs the following:

Coal	0.22	cents per k. w. hour.
Operating labor	0.10	“ “ “ “
Oil, waste, etc.	0.03	“ “ “ “
Maintenance and repairs	0.09	“ “ “ “
Total	0.44	“ “ “ “

This is equivalent to $38.54 per k. w. year of 8,760 hours. Adding this operating cost to the fixed charges of $27.00 per k. w. year, gives, for the total power cost of such a gas plant, $65.54 per k. w. year, which is somewhat less than obtained with a very much larger steam station of economical design. The saving in total power costs will be even more for smaller stations; steam and gas of the same size as the gas power costs do not vary much with size, while steam power costs do. It is also interesting to note, in this comparison, that the considerable excess in first cost in the gas power stations is over-balanced by the economy of operating power costs so as to bring the total less than for the steam station.

These costs may now be summarized for comparison, as follows:

Comparison of power costs on assumed conditions; stations consisting of six units, two in reserve and four working on twenty-four hours rated load, with the exception of the water-power. First cost and fixed charges are based on the capacity of 150 per cent. of the output.

	Water Power	Oil Engines	Gas Engine & Producer.	Steam Plant.
First cost per k. w. rating	$75.00—$200.00	160 k.w. units $217.00	600 k.w. $270.00	5000 k.w. $110.00—150.00
Fixed charges, rate per cent. . . .	10 per cent.	10 per cent.	10 per cent.	10 per cent.
Fixed charges per k.w. year . . .	$7.50—$20.00	$21.70	$27.00	$16.50—$22.50
Operating and Mfg. Costs per k.w. year	$1.00—$5.00	$56.94	$38.54	$52.50
Total power costs per k.w. year. . .	$8.50—$25.00	$78.64	$65.54	$69.00—$75.00

From these figures it appears that we have not yet reached the limit of cost of development of water-powers which may be advisable. It apparently would pay to spend even more money than $200, the present maximum per k. w. for water-power development, if there are no other considerations entering. Among the chief consideratons of this kind may be set down that of transportation of products from the works and raw material to the works, but this must be considered against the question of transmission of current from the water fall to a convenient point of transportation.

It is interesting to note how close is the cost competition of the three fuel systems for the conditions assumed for each.

Excluding the water-power plants, the first cost of the steam plants will be least, oil second, and gas engine greatest, with the fixed charges in proportion. As oil fuel is very much more expensive than coal, when referred to the heat contents, and the thermal efficiency of the oil engine not proportionately greater, it follows that the fuel element in power costs will be greater than for the steam or gas plants, except when small and load intermittent. This fuel element will always be less for gas plants than for steam when the same coal is available for both. This fact, compared with the increased fixed charges for gas plants, makes it likely that gas power will be cheaper than steam when the load factor is large, and the difference will be greater the greater the cost of coal. Smaller units in every case will have the effect of increasing labor cost per k. w. hour, but not in proportion to size reduction. Oil, waste, miscellaneous supplies, and maintenance and repairs will depend on the complication of apparatus, its service, and the quality of labor employed, but its value is problematic and cannot be predicted, except by experience with similar apparatus, which gives figures on which to base estimates.

As was pointed out in the beginning, the whole question is an extremely complicated one and requires the fullest discussion for even a fair understanding of the nature of the case, and I sincerely hope that such a discussion will be forthcoming.

DISCUSSION.

Mr. F. G. Clark: The speaker has listened with interest to the reading of Dr. Lucke's paper, and is glad to see such important comparative costs made available for general use. The costs are apparently conservative, and with due allowances for the peculiar conditions of any given case, should furnish a manufacturer a basis for rough or preliminary estimates.

The speaker agrees with Mr. Stott that knowledge of the load factor to be expected is essential to a proper comparison of costs. Generally, electrochemical works have a very steady 24-hour load, and therefore a load factor of approximately 100 per cent. Such a load will enable one to go to almost any limit in first costs to secure the lowest possible operating cost, as the fixed charges could hardly exceed 30 per cent. in a power plant of any size.

The speaker is referring to steam costs, being unfamiliar with the other costs. A factory running nine or ten hours a day, with a noon stop, has a load factor per year comparable with that of a traction power-station, except that the fluctuations of the latter are practically eliminated. The load factor would be from 30 to 50 per cent., with 40 as a fair average. In this case the fixed charges are about 36 per cent. of the total cost, and were the load factor 18 per cent. the fixed charges would equal the operating cost of power, when the equipment is installed at the usual cost and 10 per cent. taken for the fixed charges.

The speaker would refer to Dr. Lucke's steam figures as ultra conservative for an ordinary electrochemical works at 100 per cent. load factor and high for a large traction station at 40 per cent. load factor, and will give you the following estimates at different load factors of the cost per k. w. year, based on a power station equipped with 5,500 k. w. Turbo generators.

Load factor		100	80	60	40	20
Total cost		$35	40	49	65	100
Per cent.	Investment	26	29	31	36	46
	Coal	53	54	53	49	39
	Labor	12	9	9	9	9
	Misc.	9	8	7	6	6

The speaker has supposed that gas engines using producer gas were able to produce power at considerably less cost than steam, where the average load factor was high, and is rather surprised at the figures given.

We have heard a great deal about the ability of storage batteries to effect considerable saving in the first cost and the operating cost when there were peak loads lasting less than, say, two hours. When insurance is essential, the battery installation may be given a further excuse, as stated. Interruptions of service are not to be sought, but are not very grave accidents when duration is short and occurrence infrequent.

The effect claimed by the battery people in carrying peak loads can, however, be obtained at about 5 per cent. of their cost. It is of small moment how much the output costs for this short interval of time, as its average is taken throughout the day. If, therefore, the turbine be worked to its overload limit and some means be provided to increase the normal overload limit of the boilers, a large part of the saving claimed for the battery will accrue to the station apparatus. Thermal storage presents to the power-station engineer a means for cutting off the feed during peaks and replacing at times of light load, and, under ordinary power-station conditions, enables about 15 per cent. greater load on the boiler during the periods of heavy loads.

MR. JOSEPH BIJUR: As in accord with the figures presented by Prof. Lucke, I would like to remark that a steam plant with which I have had something to do recently, has figured out at about $150 per k. w. of generating machinery, including the cost of the building, for an economical condensing type of plant, which, however, does not go into refinement of automatic stokers and surface condensers. It may be interesting to note that in this case, where the units were of moderate size—that is, 150 k. w. each—the condensing steam engine appears to be more economical at all loads than the steam turbine, the percentage of economy favoring the steam engine about evenly throughout its whole low range and being quite considerable. The high cost of oil and gas engines per k. w. and their inability to stand overload successfully, point to the advisability of using a storage battery, in connection with such machinery, to handle the excess over the average load.

The storage battery costs complete, erected, much less than gas and oil machinery—probably in the neighborhood of $75 to $90 per k. w., depending upon conditions. This reduces the first cost very greatly; it enables the economical gas engine to be used to handle very fluctuating loads without making the engine larger than necessary to handle the average load continuously, and it provides a reserve to handle the load in case of accidental stoppages of the gas machinery from any of the several causes which occasionally interrupts its running for short periods, such as igniter troubles and others.

I am inclined to believe that the use of gas engines with storage battery auxiliaries will prove to be the most economical method of generating electrical power. In this connection, I should like to point out that while the efficiency of storage batteries, when storing energy for long periods, is, under conditions of practice, probably in the neighborhood of 75 per cent., it is very much higher under conditions in which the battery alternately gives and receives energy impulses, in which case the efficiency of a properly designed storage battery and efficient booster system may easily be 90 per cent. and higher. Add to this the fact that only a fraction of the total energy is handled by the battery, and you can see that the slight loss of the total energy generated will be more than compensated by the increased efficiency of the generating units working under steady load.

As a matter of experience, a decided economy in fuel results from the use of a battery, and on account of the enormous overload capacity of the latter, a flexible system is obtained at lower first cost.

DR. L. H. BAEKELAND: There are few industrial questions which are so imperfectly known as "the real cost of power production." Calculating this cost does not involve merely a question of engineering, but also that of good bookkeeping. For that reason, many mistakes have been made. Some of the statements, made by otherwise very competent men as engineers, show on their face that their estimates are erroneously low. If power could be produced by them at anything like as cheaply as they think they are able to do, then I would advise the gentlemen to give up their chemical and electrochemical enterprises, and engage in the more lucrative business of furnishing power to traction and illuminating companies.

In our discussion to-night, something ought to be said from the standpoint of the power consumer, or the man who hires power from big companies. Water power is a nice thing to possess—from the power owners' or landlords' standpoint. But, if you will examine matters closely, you will find that, after everything is taken into consideration, the full cost at which leased water power is sold to the consumer is so arranged as to meet rather closely the price at which power could be generated by other means. When I say "full cost," I do not merely mean the price at which horse-power is charged to the consumer. In the matter of cost, we should not forget that power companies receive from him who hires power other benefits than the mere horse-power rate price. Almost all of these companies realize much more profit from the increased value of the real estate they control. Whenever the question of horse-power rates is discussed, they try to mislead the consumer by ever repeating that the power company is not making any money and is not paying any dividends. They studiously omit to mention that the power enterprise is simply a pretext for a huge land speculation, which is run as a side line by the same capitalists who are interested in the power company. The power company might go on several years and "make no money," or omit paying dividends on a water-power plant, and yet increase the value of the real estate in gigantic proportions. Some of these companies refuse to sell any land outright, and merely lease it for a short term of years, with the express condition that if at any period a stipulated sum of money is not paid annually for power, all buildings and other improvements on the land revert to the power company.

Such contracts are extraordinarily hard on new enterprises, and one single unprosperous year may put the power consumer at the mercy of the power producer.

The State, in granting franchises for power development from natural resources to private companies, has unwittingly helped to build up immense land monopolies.

MR. C. O. MAILLOUX mentioned an instance where the price of power per horse-power was very high, notwithstanding the fact that water power was used. The case was that of a plant in Arizona, where the electric company paid an irrigation company for the right to use the water at the rate of about $40 per k. w. year. However, as coal of relatively poor quality cost $10, or more, per ton, the electric company could still make money, in spite of the fact that this relatively large sum had to be added to the interest on the cost of the equipment and also to the operating expenses. In Jerome, Ariz., where the copper mines owned by Mr. W. A. Clark are located, the price of $50 per horse-power year, mentioned by a company that contemplated developing a certain water power in that region, was considered a reasonable and somewhat low price, this being due, of course, to the high price of fuel, which brought the cost of the horse-power year, when produced by steam, to nearly $100.

MR. E. J. BERG: I have been very much interested in Prof. Lucke's comparison of cost of power, and appreciate the difficulties which he met in trying to make a comparison which will be of general nature.

I judge that since Prof. Lucke has worked his figures on the basis of a load factor of 100 per cent., that such load factor is usually met with in electrochemical industries; this is, however, rarely the case in any other branch of industry. Therefore, the figures, to be applicable to the average installation, would have to be very considerably modified.

There is one thing regarding the comparison which strikes me forcibly, and that is that Prof. Lucke assumes the same percentage reserved units in the three cases. I think it is safe to say that with the present state of the art, gas engines, to be operated economically, have to run within 10 to 20 per cent. of the maximum output, whereas the steam turbines are designed to give approximately double load in an emergency for a considerable length of time. I appreciate that it might be possible to reconstruct the governor device and the valve arrangement of gas engines to improve them in this respect, but I am now discussing the present stage of art. It seems, therefore, that the addition of 50 per cent. more than normal rating in gas engine units would not give more reserved power than the rated full load, in the case of steam turbines. Introducing this feature in Prof. Lucke's discussion will, of course, greatly improve the showing of the turbine.

I would also like to take exception to Prof. Lucke's statement that steam engines require less water than turbines. I think it has been demonstrated beyond question, in a large number of turbine stations installed at present time, that this is not the case, except possibly in stations involving only very small units—that is, units up to 50 or 100 k. w.

The turbine is, of course, largely a unit suitable for condensing operation, whereas the reciprocating engine might have higher efficiency when operating non-condensing.

I am very much interested in Mr. Stott's discussion about the effect of load factor, and heartily agree with him. I believe, however, that his statement that turbines are less efficient at half load than reciprocating engines, on account of the sleeve leakage, is a little bit too general, since with the Curtis turbine no appreciable leakage exists. As a matter of fact, in comparisons made it has been found that the turbines are more efficient at light loads and at overload, but there are cases where the reciprocating engine is more efficient just at the full load point.

After a thorough investigation of the characteristics of the Curtis turbine (with which I am personally familiar), there can be no question but that even with a full load efficiency slightly higher the reciprocating engine is less economical when operating over considerable variation of load. In addition to this gain in average efficiency, there is very considerable saving in the wages of the attendants in the turbo stations, compared with the stations using reciprocating engines.

MR. PHILIP TORCHIO: If Prof. Lucke would permit, we would suggest that cost of power were figured also on the basis of k. w. hour for different load factors. From the latest census report, year 1902, the average load factor of all United States lighting systems was about 23 per cent., while the street railways had a load factor of about 30 per cent., an average of all electric light and railway systems of 26 per cent.

Regarding storage batteries with high tension current supply, they are considered as an absolute necessity wherever continuity of service is of foremost importance. The batteries are then discharged at very heavy rate, so as to tide the distributing system over any momentary shut-down of the high tension supply.

The speaker begs to take issue with Mr. Bijur as to savings attained by the use of storage batteries in conjunction with shutting down engines, barring the case of very sudden and heavily fluctuating loads, as met, for instance, in some railroad services. In most other cases, purely considerations of economy would greatly outweigh in favor of mechanical power from coal than chemical power from lead.

MR. P. R. MOSES: The paper presented by Dr. Lucke is really a discussion of the comparative costs of operation of four types of plant under theoretical conditions of a 24-hour continuous full load. As has been pointed out by several speakers, this condition is one rarely approached in practice, and the load conditions, varying as they do from an average load as low as 30 per cent. of the full load capacity up to 70 per cent. or 80 per cent., have a most important bearing on the comparison of costs.

This has been already fully discussed, and I will not repeat, but there is another point which has even more effect on the operating cost than the load factor, viz., the value of the by-products of power manufacture and the use of by-products of other manufacturing processes for the production of power. Among the more important of these by-products of power manufacture are exhaust, or spent steam, from engines, containing available heat, hot water, tar and ammonia, and exhaust gases from gas and oil engines.

The exhaust steam is the most important of these by-products, because of the prevalence of the steam engine. It contains 75 per cent., and more, of the total heat units in the steam delivered to the engines, and this heat can be used for many purposes, such as evaporation of liquids, drying and heating, either directly or indirectly by some transmitting medium, such as water or air. In industries such as those of salt and sugar manufacture, the use of exhaust steam is of paramount importance, and no other means of generating power would be worth considering, as all the steam used by the engines may be again used for evaporation, thus obtaining all the heat value of the fuel not wasted in chimney gases. In other cases, such as dyeing and bleaching, the value of the exhaust steam for heating the buildings and furnishing hot water is of equal importance, and places the steam engine safely ahead of water power or gas engines.

The tar and ammonia by-products of the gasification of fuel offer in large installations opportunities for saving in operating cost, and affect in large measure the choice of type of power plant.

On the other hand, the by-products of other manufacturing processes may have an equally important bearing on the choice of plant; as, for example, the bagasse or refuse sugar cane is a good fuel to burn under steam boilers, and hence where this is available, the steam plant is indicated.

In blast furnaces the availability of waste blast gases for use in gas engines points to the gas engine as the desirable plant.

In the saw mill the cheap and plentiful supply of waste wood indicates the use of steam power.

In the great majority of cases, the consideration of the value of the by-products, or the availability of by-products of other manufacturing processes, will be found to have more to do with the decision as to the kind of plant to be installed than the comparative economy of the various types under assumed theoretical conditons. Each case must be studied individually, the actual probable load factor determined, and tabular statement made up, showing the costs of installation and operation with each type of plant, making proper allowance for value of by-products.

MR. EMMETT: The accompanying curves illustrate the results accomplished by the Curtis turbine in the highest state of development which it has so far reached, and will be of interest in connection with the subjects discussed at this meeting.

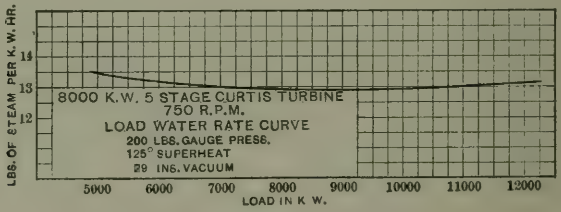

FIG. 1.

The first curve shows the performance of an 8,000 k. w. turbine at different loads, with a moderate degree of superheat and high vacuum. These conditions correspond closely to those which are being commercially obtained in different large plants where these turbines were installed.

The second set of curves shows a comparison of the performance of the 5,000 k. w. Curtis turbine with a reciprocating engine of the same capacity of the type operated by the Interborough Metropolitan Co.

The results produced by these machines show the best steam efficiency that I have seen reported. The 8,000 k. w. machine, operating with a 28-inch vacuum, delivers to the shaft 71 per cent. of the total available energy in the steam. Other steam engines have given better efficiency for certain thermal ranges, but not for a range extending to such a high degree of vacuum.

In additon to the advantage of this very high net economy, these machines are remarkable for their maintenance of high economy through a wide range of load, and are particularly valuable for high economy at large overload. High overload economy simply constitutes an extension of peak load capacity in station, and thus extends the range of a given investment.

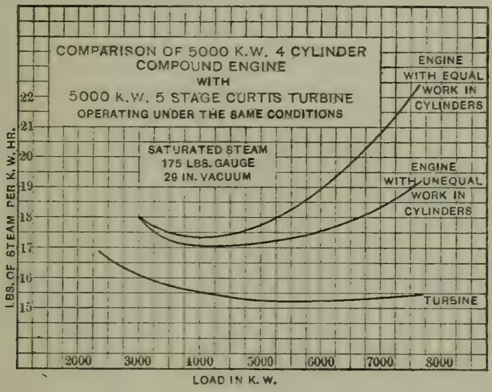

FIG. 2.

The second set of curves illustrates very well the advantage of high efficiency at overload. The engine in this case, when operating at 50 per cent. overload and with equal work in its cylinders, will consume 43 per cent. more steam than the turbine operating under similar conditions. This means that the substitution of the turbine for the engine would effect an increase of at least 40 per cent. in the peak capacity of the station without change in the boilers or other auxiliaries.

In comparing the results of these turbines with those obtainable from other prime movers, the following facts should be borne in mind:

First, that they can be operated in very large units, which fact conduces to great economy in production of power on a large scale.

Second, that the cost of installation on the maximum capacity basis is extremely low.

The peak capacity of the 8,000 k. w. unit above referred to can be put at about 14,000 k. w., and the unit can be easily equipped with a generator which will carry this load continuously. Machines of this type in the station of the Commonwealth Electric Co., at Chicago, have been repeatedly operated at 14,000 k. w. from the group of eight 520 horse-power boilers which is assigned to each. If we rate such an equipment at 14,000 k. w., the cost, with the most expensive construction, will not exceed $45 a kilowatt. This unit, when operating at 14,000 k. w., is not more than 5 per cent. below its full load efficiency, and is consequently available for economical daily operation at such a load.

This machine is capable of delivering in the form of electric power 20 per cent. of the total heat energy carried by the steam which it uses. From experiences of actual operation, it is estimated that under conditions existing in our large cities, power can be produced on a large scale in these units at a cost of 0.25 cents per k. w. hour. In comparing these results with those obtainable from gas engines, this cost must be considered, rather than any comparisons of thermal economy. This turbine development conduces to the wholesale production of electric power from coal by simple and practical means, and its merits cannot be appreciated without reference to this idea.

It is probable that further improvements will be made in the economies of large turbine units. It is not probable, however, that these improvements will be of very radical importance, since the limits are being approached. There seems to be a large scope for improvement in the design of boilers for such wholesale steam production, and I look for considerable advances in this direction.

(*Communicated.*)

Prof. M. Namba (of Kyoto, Japan): The municipality of Kyoto operates a water-power plant developing a maximum of about 2,000 k. w., which supplies light and power service within the city. In the near future the plant will be enlarged, by the addition of about 5,000 k. w., also to be furnished by water power.

Following is the tariff of charges for power, on the basis of 12 hours service per day:

Under	5		H. P.	$47.50	per H. P. per year
Between	5 and	10	H. P.	39.00	" " " "
"	10 "	20	"	36.00	" " " "
"	20 "	30	"	33.00	" " " "
"	30 "	50	"	28.50	" " " "
"	50 "	100	"	26.50	" " " "
Above		100	"	24.00	" " " "

For service between 10 and 12 hours a proportional reduction is made, and a proportional increase for service between 12 and 14 hours; for 15 hours the increase is 30 per cent. over the 12-hour rate, and above 15 hours the increase is 50 per cent.

Discussion Continued at the Eleventh Annual Meeting of the Society, Philadelphia, May 4, 1907.

MR. SPERRY: I don't like to take up so much time, but there are two or three things in Dr. Lucke's paper and in the discussions that follow that it might be wise for us to have in mind; for instance, by turning to the discussion by Mr. Emmett, you will notice that he gives power costs (under conditions which he states were actual, and actually realized in the West, with coal that I think runs about $1.90 to $2.30 per ton) of $16.10 a horsepower year, whence, by calculation, we find that the thermal efficiency is about 14.2, converting simply 14.2 per cent. of the available energy of the coal into actual power.

There have been a great many different estimates given of power costs. Dr. Lucke seems to be about the head of the list, so far as high power costs are concerned, and our right worthy member, Dr. Hutton, over in England, about the foot of the list. He is down extremely low—so low that I am afraid they cannot be realized.

We have in this country one very large power station in the new line, namely, gas engines and the large gas-driven electrical units, in operation at the Lackawanna steel plant. There we have a blast furnace operation on a large scale, sufficiently large, so that we ought to be able to find out something as to where our power costs are going in the future. Quite considerable information has been gained from this operation.

Dr. Lucke gives several values here which, it seems to me, are too high. The several items of cost have been figured time and time again on these points, and they come not far from $20, while there are two calculations under $20; these items are outside of fuel costs. This is interesting—that a large plant, laid down on an extensive basis as they are, can be operated outside of the fuel cost, in the neighborhood of $20. That is on the Niagara basis, you see; then, Dr. Lucke himself states the fuel factor, the coal consumption with $3 coal would introduce another item of $13, making $33 for a horse-power year, or $44 per k.w. year. This is important, as the plant has been installed on fixed charges that are much higher than some plants will be in the future.

To go one step further into the future, and see what reduction we will possibly be able to secure when we come to compound gas engines, we are now able to cut down the fuel supply to something nearly where it ought to be; you understand that the last large contract for gas engines went in under a guarantee of about 11,000 thermal units per horse-power hour, whereas power has been obtained in the neighborhood of 6,000 thermal units per horse-power hour, and in future we may expect something of the order of 6,000 thermal units per delivered horse-power hour. On this basis, our $33 will be reduced, with all the factors in it, to $24 or $32 per k.w. year. Those are not far from figures that we will have to encounter and deal with in the future.

Mr. Charles E. Lucke: Several speakers in the discussion have referred to the importance of considering load factor in studying power costs. There is absolutely no doubt about this point, as was referred to in the main body of the paper, and 100 per cent. load factor was used in the computations, first as a matter of convenience, and secondly because it was believed that electrochemists, whose load is practically constant, will be more interested in the 100 per cent. load factor than in the others. Should anyone be interested in computing the effect that might be expected from the change in load factor on the cost given, he may keep the fixed charges constant and assume any proportion of the operating charges given.

Another matter that has been referred to is the question of rating versus overload capacity of units and the efficiency of units at various loads. The rating of the unit is a purely arbitrary procedure, and it may be rated at its most economic load, in which case the first cost per horse-power will be high, or it may be rated at its maximum overload, at which the first cost per horse-power will be low and the efficiency correspondingly poorer. Just where to rate a unit is a question decided by every manufacturer by himself, and it frequently happens that when customers demand low prices the rates are changed in bidding. It is not as true as one speaker seemed to feel, that the greater the overload capacity of a unit, the less reserve units are needed, because a reserve unit is not only valuable for its capacity to carry some load, but is also, and even more, useful for the opportunity which offers for the shutting down of a unit that may be in need of repairs. In carrying a twenty-four hour steady load, reserve units are needed only for the latter purpose, so it makes very little difference whether a given unit has much overload capacity or none at all. This particular feature for the turbine becomes important only when loads are violently fluctuating and the fluctuations sudden, a situation which is never met with in electrochemical loads. I have been particularly interested in the discussion presented by Mr. Emmett, because of the quantitative nature of the data he gives. His comparison of the reciprocating units and the Curtis turbine water rates is extremely interesting, and I hope, but rather doubt, that the relation of the water rate of these two units will be the same in the general run of power work. His estimate of 2½ mills per kw. hour for turbine stations is extremely low, and, personally, I do not believe it possible. I should like very much, indeed, to have the opportunity of examining the records of any station that could have such power costs as this. If it is in existence, it should be widely advertised, because it is a remarkably fine performance, and one many power plant owners would like to reproduce.

In conclusion, I should like to urge upon all owners of plants the importance of keeping accurate records of costs, including both fixed and operating charges, and of giving them to the general public for comparison. It seems to me that power costs should be considered purely engineering data, just as water rates and boiler efficiencies are, and that it is about time the strictly business attitude of cost secrecy was abandoned.

A paper read at the Eleventh General Meeting of the American Electrochemical Society, at Philadelphia, Pa., May 4, 1907, President Carl Hering in the chair.

ELECTROCHEMICAL PROCESSES AS STATION LOAD EQUALIZERS.

Reply to paper by E. A. Sperry.*

By John Meyer.

Mr. Sperry has very ably discussed the station managers' viewpoint of this important subject, which involves peak conditions, availability of service, rates and cut-off privileges, all of which must be considered. It is to be regretted that he did not discuss at length the operating conditions or requirements of the electrochemist and electrometallurgist, thus furnishing the station manager with some idea of the scope of the work. With these requirements applied to his conditions, certainly some tangible result would obtain. The writer will endeavor to place before you the commercial aspect of this subject from the Central Station viewpoint, with the hope that the electrochemist and the electrometallurgist will give this matter further consideration.

Costs.

The final location of a plant for electrolytic or metallurgical processes, not unlike manufacturing, will result from the knowledge of all costs involved in the process, and not alone the cost of current. To illustrate: A large Philadelphia concern desired a location for its manufacturing plant. Several water-power sites were examined, including Niagara Falls. It was decided, after a careful analysis of all costs (and in the face of cheap water power), to erect the plant in Philadelphia. The actual power cost, as determined by several years' actual operation, indicates that if the lighting company had had the existing rates in force at the time the steam plant was decided upon, the. plant installation would never have been made. It would appear, therefore, that the cost of power is not the deciding factor.

Assume the intention to erect a plant for the production of a

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* Trans. American Electrochemical Society, IX (1906), p. 147.

commodity which we will call "X." The following schedule shows graphically the several items which should be considered:

- **Cost to Produce and sell "X"**
  - **Production Cost**
    - **Material**
      - **Raw Material**
      - **Finished Commodity**
      - **Accessories**
      - **Transportation**
        - **Freight**
        - **Express**
        - **Drayage**
    - **Labor**
    - **Burden**
      - **Power**
      - **Rent, heat, light**
      - **Taxes**
      - **Insurance**
      - **Depreciation**
      - **Maintenance**
  - **Selling Expense**
    - **Office**
    - **Salesman**
    - **Estimating**
    - **Advertising**
    - **Traveling**
    - **Indirect**

In this analysis neither the selling price nor the profit will be considered, upon the assumption that the selling price is fixed by the law of supply and demand, and the profit will presumably be the difference between the cost to produce and sell and the selling price.

Mr. C. J. Russell, of the Philadelphia Electric Co., has given considerable thought to this subject, and in his paper read before the Association of Edison Illuminating Companies, in 1906, indicated several important points which should be considered in discussing this matter, namely:

"While the tendency seems to be to locate such industries where water power is available, there are other factors which may help the central station to secure consideration in the matter of current supply. The question of facility and low cost of transportation of raw materials and the location of principal market centers for finished product are important to any industry.

"There are some electrochemical industries located now in out-of-the-way places which could obtain better results near some of our great shipping centers, for the reason that the cost of transportation of raw and finished product plus the loss of certain by-products which cannot now be utilized, more than offsets the advantages gained by the price of electricity at the present location.

"While water power may seem reasonable, these items of expense may make central station service in some other and more favored locality the cheaper in the end."

An investigation, as outlined above, may prove it more desirable to locate an electrolytic plant in Philadelphia in preference to Niagara Falls or elsewhere where such low rates have been quoted. Assuming such to be the case, the problem is then reduced to a comparison between the power costs of central station supply *versus* isolated plant.

The items enumerated below are those that can generally be considered as making up the total cost of operating an isolated plant:

Salary of engineers.
Salary of firemen.
Salary of electricians.
Fuel.
Removal of ashes.
Water.
Repairs to boilers, engines, and dynamos.
Tool account.
Miscellaneous expense.
Supplies, oil, and waste.
General expense.
Depreciation.
Interest in investment.
Insurance—fire and boiler.
Rental value of space occupied by plant.
Liability insurance.
Taxes.

Having obtained the total operating cost, we invariably but erroneously divide this cost by the capacity of the boiler, engine, or generator, and obtain a cost per horse-power or per kilowatt per annum. Either result divided by 8,760 hours produces a rate per horse-power hour or per kilowatt hour. Undoubtedly, the cost per kilowatt hour is the only correct basis for comparison. However, the foregoing method of arriving at the cost per kilowatt hour is incorrect, inasmuch as it does not consider the relation between the theoretical and the actual power generated.

The theoretical kilowatt hours per annum may be found by multiplying 8,760 hours by the rated kilowatt capacity of the generator, or the maximum amperes by volts when all the cells or other apparatus are in service.

The actual kilowatt hours per annum will be a modification of the theoretical kilowatt hours depending upon the time lost in repairs to or overhauling of furnaces, cells, etc. It may be obtained fairly accurately by multiplying the number of pounds of "X" produced in any year by the watts hours required to produce one pound. Dividing the total power cost by actual kilowatt hours thus obtained will probably produce a rate comparable with, if not higher than, the rate named by the central station.

The fixed charges on the investment necessary to carry the electrolytic load over the Central Station peak must be considered in making rates. With this peak factor eliminated, lower rates could be named.

In conclusion, I desire to add that central station managers in general are anxious to coöperate with such desirable business, and are open to any suggestions that may solve the problem. A great deal of good would result if a committee were appointed, consisting of the interested parties, with instructions to investigate and report at your next meeting.

DISCUSSION.

MR. A. A. SPERRY: I am very glad that the matter has been taken up further. I have felt for some years that some progress ought to be making along this line. I do not believe, myself, that the time is ripe yet; because, as I stated in my paper, we do not seem to be found ready with intermittent loads. The whole point of equalizing, as was intimated in the paper here, consists entirely on being able to take the load when in the valleys; and I might state, in that connection, that the valleys are very much more serious in character than people ordinarily understand; as the last census shows that the average load factor or the load on the stations of the United States is only about 26 per cent., and there is nearly 75 per cent. to be filled up; and we, as electrochemists, should work along the lines laid out in my paper, and suggested by all who have been interested in this subject, namely: We should try to develop electrochemical, or more especially electrical furnace and metallurgical processes which will fit the comparatively short periods of current supply available. Dr. J. W. Richards mentioned, last year, one process which took nineteen hours for its completion. Processes of this general character are what are needed to utilize these idle power plants at full efficiency.

Now, in considering the future, the more remote future possibly, we are going to load up our water powers, we are going to load up our blast furnaces, and, of course, it goes without saying that we are going to reach out and lay hold of practically all of the various electric generating facilities we have in this country that are idle and have the available generating capacity. The fixation of nitrogen and the other great problems lie before us and must be solved by the electrochemist and the metallurgist, and as these are solved we are going to utilize such power as lies around loose, regardless as to whether nature furnishes it to us or capitalists furnish it in the shape of idle machinery. Let us join hands in reaching this point as soon as possible. It will all tend to quite considerably reduce the power cost to everyone concerned.

I am glad that Mr. Meyer made the suggestion he did after reading the paper. It is barely possible, though, we might not be able to accomplish so very much just for the immediate future; yet this art has grown very rapidly, indeed, and no one can say just how soon we may be ready to take part of the load and help equalize the load of some of our larger stations. In any event, the report of a committee such as he proposes, and which was discussed to some extent last night, will be able to set a milestone, and might help the people that follow on after to know where we were at this particular juncture; they would certainly be able to accumulate and tabulate data from which very valuable results might follow. I am quite heartily in favor of some such action, if it would seem to be in accordance with the general idea of the Society.

Mr. E. R. Taylor: I regret, exceedingly, that this paper has come at the very end of what we have to say to-day. It is exceedingly important, the power for electrochemical industries. I don't feel like taking the time that I would like to take in this closing hour, but I do want to say just a word, with your permission.

We need, as electrochemists, to get as close to Mother Nature as we possibly can; and we cannot get there when we are compelled to buy our power of somebody else. It is all well enough, in starting things, to do that; and yet, I got bit from $16,000 to $20,000 in a matter of that kind myself; and it set me back a long time. We have an example of a grand industry at Niagara Falls, recently, which had paid a power company about $500,000 for power—a sum sufficient to equip themselves with a grand water-power—and they were the first to lie on their backs when a fire overtook them. We need to get at Mother Nature just as quick as we can, for the largest developments of power, and it will cost us less; but for some things we ought to be able to get a great help, as indicated in the paper of Mr. Meyer, also by Mr. Sperry. I hope that we may have something said at a future meeting when there is more time. I do not feel justified in taking another moment of your time to-day.

A paper read at the Eleventh General Meeting of the American Electrochemical Society, in Philadelphia, Pa., May 4, 1907; President Carl Hering in the chair.

THE HELION LAMP.

By H. C. Parker.

The Helion lamp, now exhibited before the Electrochemical Society, is the result of a number of years of experimenting on materials for incandescent lamp filaments by myself and Mr. Walter G. Clark, an electrical engineer from the Pacific Coast.

For the past three years the research work has been carried on in one of the research laboratories in Fayerweather Hall. We have for a number of years directed our attention to the development of a material capable of withstanding a higher temperature than the carbon filament used in the incandescent lamp. The carbon filament at present used begins to disintegrate or vaporize at a comparatively low temperature, when that temperature is produced by a passage of an electric current through the filament, the disintegration beginning between 1400° and 1600° (black body temperature), and by the time 1700° (black body temperature) is reached, the disintegration is so rapid that the lamp fails, either through the filament parting or through loss of efficiency, due to the disintegration of the filament and the deposit upon the glass of the carbon shot off or vaporized from the filament, so with the ordinary 3½-Watt carbon filament lamp the efficient life of the lamp is taken at approximately six hundred hours, for if the filament does not part at this time the efficiency has dropped to a point where it is more economical to pay for a new lamp than to pay for the increased current consumption per candle-power of light delivered.

Another feature of incandescent lighting is the yellow color of the light, which does not give the same color values as daylight. For this reason, colors appear very differently when observed under daylight and the incandescent electric lamp, and for the same reason a lamp giving a light more nearly the color of daylight is a more effective illuminant, as the human eye has become trained to observe and judge colors and illumination under solar light.

As the temperature of a solid-body source of light increases, the proportion of blue and violet rays increases more rapidly than the longer waves in the red and yellow end of the spectrum. For this reason, the red and yellow become less prominent, and the light becomes whiter as the temperature increases.

The matter of selective radiation can also be utilized to this end when the selective radiation is in that portion of the spectrum which tends to produce a light approaching a white light, of which the Welsbach mantle is an excellent example of selective radiation in this portion of the spectrum. The Cooper-Hewitt mercury vapor lamp is another illustration of selective radiation, but from a gas; in this case the selective radiation is in the blue and green end of the spectrum and is lacking in the red and yellow rays, so that the light produced is very different from sunlight.

In the development of the Helion filament, we experimented with a great many substances, covering practically every element whose physical properties gave any promise of success, in both metallic and non-metallic elements, and we became convinced that while some metallic substances would withstand the temperature necessary to produce an efficient filament, the low resistance of metals would necessitate that the filaments should be of exceedingly small cross-section in order to secure sufficient resistance to properly utilize the voltage of an ordinary commercial circuit in a lamp of any modern or commercial size.

It is exceedingly difficult to produce a filament from the refractory metals of the small cross-section necessitated by the high conductivity of the metal, and if the filament is produced, it is so attenuated that it is lacking in structural strength, so that a lamp made from this character of filament would be exceedingly fragile.

Our only observations along this line have been born out by the difficulty experienced in producing commercially a practical metallic filament lamp for commercial voltages. In producing a lamp filament from material of lower conductivity or higher resistance than a metal, it is possible to use a greater cross-section for a given degree of incandescence at a given flow of current.

Some early experiments by Mr. Clark indicated silicon as a material which gave promise of considerable success, although the melting point of this material was comparatively low, but we found that under certain special conditions we were able to produce the material in such a condition that it withstood vaporization to a very high temperature, and we also found that the radiation in the visible spectrum was greater than that of the ordinary carbon filament.

This increased radiation was not confined to one portion of the spectrum, but appeared to extend throughout the entire visible range, and gave promise both in the matter of withstanding higher temperatures and in giving off a greater percentage of wave lengths in the visible spectrum than any other material with which we had experimented so far. We have experimented upon this material for several years, and, after repeated failures, we succeeded in producing the desired material in the form of a filament possessing the necessary characteristics for use in an incandescent lamp.

The method by which the filament is made is very similar to the one used in treating or flashing the ordinary carbon filament, as we use a base of carbon very similar to the ordinary filament, on which we deposit a silicon compound out of gases, which are introduced into a flask of the same general type as used in producing a carbon filament. As soon as the material begins to deposit upon the surface of the filament, the emissivity in the visible range immediately increases, and, with practically no change in the current consumption, the brilliancy increases very materially. The permanency or life of the filament at the temperature at which we operate is apparently dependent upon the amount of the compound which is deposited upon the filament, but when a sufficient amount is deposited, we still retain a resistance high enough so that we are able to absorb 110 volts in a single corrugated loop.

We have been able to produce lamps of this character for 110 volts consuming 30 Watts, giving 30 candle-power of light, and withstanding a temperature of 1750° (black body measurements) without any apparent disintegration or blackening of the globe.

Another characteristic of the filament is that, while the material applied to the filament in our treatment has a negative temperature coefficient of resistance and the carbon on which it is deposited has a negative temperature coefficient, the completed filament exhibits this negative temperature coefficient only to about 1400° (black body temperature), at which time it reverses, becomes positive, and the positive temperature coefficient increases very rapidly as the temperature increases, so that in this respect the filament has both the desirable feature of negative temperature coefficient, from the central station point of view, and a positive temperature coefficient at the temperature at which it is operated, which is valuable from the consumers' point of view, as it enables a lamp to better withstand increases of voltage than would be the case if the temperature coefficient were negative.

To test the efficiency of our lamp, candle-power determinations on both the carbon filament and the Helion filament were made by the Electrical Testing Laboratories. The temperature determinations were made on the same lamps by means of the Fery absorption pyrometer, at Columbia University. It was found that the carbon filament lamp at 1380° (black body temperature) required practically 9 Watts per candle-power, while the Helion filament at this temperature required but 3½ Watts. At 1500° (black body temperature) the carbon filaments required 3⅔ Watts per candle-power, the Helion filaments, 2⅓ Watts per candle-power.

The carbon filament lamp was rated at 3½ Watts per candle-power. At this rating, the temperature observed on the pyrometer was 1510°; at 1600° the carbon filament lamp required 2¼ Watts per candle, the Helion, 1½ Watts per candle-power.

At this temperature the disintegration of the carbon filament was so rapid that the efficiency began to fall off very materially before another reading could be made, but the Helion filament was carried up to 1700° (black body temperature), at which temperature it consumed 1.07 Watts per candle-power. In raising the temperature on these filaments from 1400° (black body temperature) to 1600°, the resistance of the carbon filament decreased 4 ohms, while the resistance of the Helion filaments increased 5½ ohms. From 1600° to 1700° (black body temperature) the resistance of the Helion filament increased 9 ohms.

Conclusive life tests have not been completed upon the low candle-power filaments of small cross-section, but life tests made upon filaments of greater cross-section for higher candle-power filaments at 1 Watt per candle-power, operated up to, in one case, as high as 1,270 hours, and on a number of filaments upward of 700 hours, and in each case the drop in candle-power was very small, only about 3 per cent. In each case the lamp failed at or near the joint where the filament was united to the platinum leading-in wires.

We find that the cement used for uniting the filament to the platinum acts upon the filament, so we are at the present time engaged in the development of a cement for making this joint which will not act upon the filament, as the lamps of low candle-power must necessarily have filaments of reduced cross-section, but the amount of cement used is practically as great as though the filament were of much greater cross-section. For this reason, a cement which acts upon and destroys the surface will destroy the small filament much more quickly than it does when used with a filament of greater cross-section, but our experimental lamps, produced in the laboratory, have operated under laboratory conditions at a consumption of 1 Watt and less than 1 Watt per candle-power for a period of time which encourages us in the belief that the Helion filament can be made commercially practicable at a consumption of 1 Watt per candle-power, with the added advantage that the light given by the Helion lamp is a pure white light, more nearly resembling sunlight than any artificial illuminant yet produced.

It is for this reason that we adopted the name which we gave the lamp, Helion, from *Helios.*

DISCUSSION.

MR. W. G. CLARK: One point Prof. Parker did not bring out that I think is quite interesting is the characteristic temperature curve and comparison of temperature with the light efficiency curve of the carbon filament. We take the characteristic curve of the carbon filament, apply a very thin coating of our helion or silicon material, and take the characteristic again. We find that we have increased the amount of light given off by that filament at any point of the temperature. We start in at 1300° C., where it just begins to give light, but still it gives more at that temperature than the carbon filament. When it runs up to about 1500° C., it gives very much more than the carbon filament. If we increase the percentage of coating which we apply, the light comes up directly in proportion as we increase that percentage—that is, up to a given point. In loading that filament, I have made up a curve which indicates the point at which the carbon core comes into the active current-carrying field; in other words, to begin with, the material on the surface is carrying the greater part of the current. When we have a positive temperature coefficient, if we increase the current, it finally reaches the point of maximum current density, and beyond that point we get a modification of the curve, which indicates that the carbon is carrying some current, as well as the silicon carrying the greater part of the current, because it changes over to that point. We can follow that point up or down by increasing or decreasing the amount of silicon on the surface of the filament. It made quite an interesting set of curves.

Prof. S. A. Tucker: I would like to know about the efficiency and life of the lamp—that is, whether it is as efficient, say, in candles per Watt at the end of 700 hours as it is at the end of two hours.

Mr. Clark: The last tests on the lamp are not, by any means, conclusive, but we have had lamps run up 11,270 hours; at the end of 1,230 hours the decrease in candle-power was only about 3 per cent.; other lamps ran 700 hours with decrease of about 3 per cent. Our light tests on lamps are not by any means conclusive, as, like all other people who have gone into the lamp business, we are having our own troubles with the matter of joining the filament with the platinum, and we have been focusing our attention upon that. Now, materials which did not act upon them did not seem to disintegrate them at all, or but very slightly, at the temperature at which we run; so we had quite reason to believe that we will run 500 to 700 hours with a very small reduction in candle-power. The silicon by which the carbon is surrounded apparently does not disintegrate, and does not deposit anything on the glass. This is one of the advantages, because carbon lamps deposit carbon on the glass.

Mr. Leon Gaster: I wish to congratulate the authors for their important achievements in improving the efficiency of electric incandescent lamps. Compared to carbon filaments the results are, so far obtained, highly encouraging. What I should like to ask the authors is whether they could give a detailed description of the methods adopted for measuring the temperature of the filament, and also give the curves indicating the relation between light emitted and temperature of the filament? The subject of accurately measuring the temperature of filaments is of the greatest importance for properly comparing and understanding the efficiencies obtained by the new metal filament lamps. The results so far published regarding this point do not seem to be quite corroborative, and an explanation of the methods adopted might perhaps clear up this apparent discrepancy. There is another point on which an explanation would be useful, and that is whether the authors have made sufficient tests to determine the useful life of the lamp, namely until the c. p. of the lamp dropped 20 per cent. from the original, and to indicate the relation between voltage fluctuation and light emitted. It is well known that with ordinary carbon incandescent lamps the voltage fluctuation plays a very important rôle in the steadiness of the light, and influences the life of the filament considerably. If the voltage at which the lamp is working is increased several per cent. above the one for which the lamp has been constructed, the lamp is quickly destroyed. The question of the homogeneity of the deposit on the carbon core is of considerable importance in order to guarantee uniformity of production, and I would like to ask the authors whether they have been successful in making perfectly homogeneous filaments? The characteristic feature of this new filament, of being so pliable and that the size is so reasonably small, is of very great practical importance, and represents a great advantage over most of the new metal filament lamps, some of which are very brittle in handling, and transport. The fact that on the Continent, and in particular in England, the high voltage is used for lighting purposes, should give an opportunity to this new lamp of finding a ready market, as there does not seem to be any difficulty in making 200 or 250 volt lamps, which should not be larger than the present carbon filament lamp.

I should like to know whether the authors have tested the lamp burning under direct or alternating current, and whether they found any difficulty in the use of either systems of current supplied, as it is known that some of the metal filament lamps cannot be worked conveniently on alternating current, and in particular at high frequencies.

This new lamp has no doubt very great possibilities, and I wish the inventors every success in further increasing the efficiency of incandescent lamps, contributing thereby to convert electric energy into light at a more reasonable rate than was the case up to now with the ordinary carbon incandescent lamps.

A paper read at the Eleventh General Meeting of the American Electrochemical Society, at Philadelphia, Pa., May 4, 1907, President Carl Hering in the chair.

SURFACE PROPERTIES OF ALUMINUM AND ZINC.

By William J. Hammer.

Not long ago I had the privilege of entertaining your esteemed secretary in my little laboratory, in New York, and, incidentally, showed him some experiments I was then conducting upon the molecular and surface characteristics of aluminum and zinc in connection with some professional work I had in hand, and he suggested that I present a paper upon the subject at this meeting, but I told him I feared that there was hardly time, and, furthermore, there still remained much to be done; but in view of the fact that through some misunderstanding a paper has been placed on the program as coming before this meeting and, as quite a number have spoken to me regarding the paper I was supposed to present, perhaps it will not be out of place to speak of certain lines of experimental work carried out or proposed by me, as they may prove suggestive to others investigating this interesting field. It is a field of great magnitude, and work in this direction, I feel, would most usefully supplement the work of the chemist, and particularly the electrochemist.

You are all familiar with the films of oxide which cover the surfaces of sheets of zinc and aluminum, and with the fact that this film, particularly in the case of the aluminum, will form instantly behind a tool which is cutting off the layer of oxide which formed a protecting coating to the aluminum plate. Now, in certain experiments this coating was an important factor; in others, I endeavored to secure as clean and highly polished a surface as possible, and in still other cases the metal plates, rods, etc., were prepared with a soft velvety texture to the surface by placing the objects in a tray containing *lignum vitæ* balls and powdered pumice stone and water, the tray being given an eccentric or washing motion. This and other processes employed in the lithographic arts were used in preparing the specimens. In certain of the experiments I had plates of aluminum and zinc which had been similarly treated placed in a Rowland engine and ruled with fine lines, similar to a diffraction grating; and then had microphotographs made of the ridges and hollows thus formed. In other cases scratches were made across the plates with a knife-blade, and the formation of the oxide at the summit of the ridges and in the valleys was studied, as well as the structure of the metal itself. Dr. Campbell, of Columbia, than whom no one with whom I am acquainted has greater skill and experience in microphotography, has assisted me in this portion of my work, and he has also made an interesting series of microphotographs of the various plates of both treated and untreated metal.

Another line of investigation was the pouring of various liquids upon the surfaces of the metal plates, allowing them to spread in certain cases, and studying the surface tension of the drops and the edge angles, and in other cases allowing the liquids to flow down the surfaces of the aluminum and zinc plates placed at definite inclinations. I even made miniature glaciers, which took several months to flow over the inclined plates. In some cases liquids were blown across the plates when placed on a level, and the manner in which the materials adhered to the surfaces was studied. As an illustration, I might mention that when one pours collodion upon a zinc plate it soon dries, curls up, and blows across the table, whereas a similar amount of collodion poured upon a sheet of aluminum will, upon drying, adhere so firmly that it can scarcely be removed by a knife-blade, and even then only peeled off in fragments.

In certain results, the structural formation of one metal seems to lend itself far better to the locking fast of certain substances applied to the surface, and there is a greater oxidation at the points than in the valleys, and there may be a slight mushrooming of the oxide. In certain others there is more or less of a chemical action between the metal and the substance applied. I have tried attaching flat plates of the same metals and of dissimilar metals to the shafts of electric motors and rubbing such surfaces against one another.

I have poured liquids, such as lithographic ink and color, etc., through funnels and tubes of various kinds, and in certain cases have filled dropping tubes, and after closing the top have placed the lower end of the tube many times upon the treated plates to note how much of the substance would be drawn out of the tube by the hold which the surface of the plate would have upon the viscous liquid. I have rotated these tubes and plates, covered with lithographic ink and color and other substances, by means of an electric motor, and noted the effect of centrifugal action, especially in spreading the substances over the plates.

I have dropped single drops between round rollers placed close together and revolving in opposite directions, and studied the degree with which the material would be wrapped around one metal roller as compared with the other.

In common with others, I have studied the relative opacity of the two metals to X-rays and to the rays of radium.

I have made quite a number of experiments in which similar plates of zinc, treated and untreated, were covered with lithographic ink or color, and the force necessary to pull them apart or slide them past one another was compared with similarly treated plates of aluminum. The above, together with efforts to prove absorption and porous qualities, compression of the mass of the metal, etc., and the preparation of a series of tables of the various characteristics of aluminum and zinc collated from many sources constitute the lines upon which I have worked, and I have only made these crude, impromptu remarks with the hope that they may perhaps stimulate you, gentlemen, who are possessed of so much greater ability and experience, as well as blest with superior laboratory facilities, for carrying out investigations in this promising field.

A paper read at the Eleventh General Meeting of the American Electrochemical Society, at Philadelphia, Pa., May 4, 1907, President Carl Hering in the chair.

ENERGY CHANGES ACCOMPANYING ABSORPTION.[1]

BY HARRISON E. PATTEN.

INTRODUCTION.

Absorption.—The term "absorption" is used in general to designate the process by which a solid or a liquid draws unto itself and retains within its structure, or on its surface, another solid, liquid, or gas. Where a solid retains another substance, so that the two form a homogeneous body, the mixture is either a definite chemical compound or a solid solution.

A special case of absorption has been termed "adsorption," which may be defined as the existence of a difference in concentration or density of the film adjacent to a bounding solid, and the concentration or density of the mass of the liquid or gas which bathes this solid.

Whether this absorbed film is in a liquid, solid, or gaseous state, or even loosely combined with the solid bounding medium, is not easily determined, and has been the subject of much discussion. The change of state from solid to liquid and liquid to vapor is in general very gradual. All the recent physical researches dealing even with hard, polished "solid" surfaces indicate a mobility of parts, an openness of structure, and a high power of retaining foreign material. But the ability of one body to hold another upon its surface is dependent upon the material of which each consists. Consequently, we are accustomed to say that adsorption depends upon the chemical constitution of the solid and of the substance. Another way of stating the same idea is to attribute adsorption to a specific attraction between solid and adsorbed material. It is possible, too, to view absorption as a special case of adsorption, in that where a solid imbibes a solution or a gas we have an adsorption upon the walls of the fine pores in the solid, as well as a filling of these pores

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[1] Published by permission of the Secretary of Agriculture.

by the liquid or the gas. The first four paragraphs below define more precisely four cases where purely adsorption effects may be expected, and the next three paragraphs indicate the extension of these adsorption phenomena to include cases more commonly considered absorption effects.

1. The simplest case is where a plane surface, such as glass, adsorbs a vapor or a dye from its solution. Here a regular distribution of adsorbed material between solid and vapor or between solid and solution can be shown. In A, Fig. 1, S represents the solid, and L the liquid or vapor, the concentration being indicated by shading.

2. When the surface of the solid is curved, the radius of curvature must be taken account of in discussing the effect of surface tension upon the change of concentration near this surface, and for surfaces not spherical the treatment becomes still more complicated, as the radius of curvature varies. See B, Fig. 1.

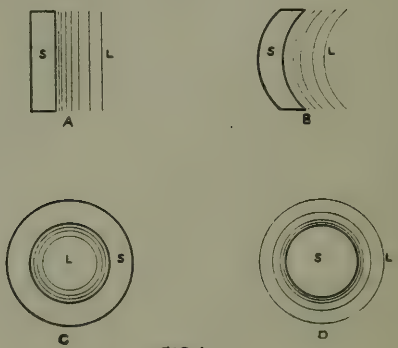

FIG. 1.

3. When the surface incloses a sphere or other form of cell, adsorption is still in evidence upon the inside wall of the cell, as shown in C, Fig. 1.

4. Conversely, a sphere or other solid body exhibits adsorption, and the curvature of its surface must be considered—D, Fig. 1.

5. Where a solution is taken up by a solid made up of cells, the total abstraction of solute from the main body of solution is produced by adsorption added to the simple filling of the cells with solution.

6. Crystalloids, as well as amorphous bodies, can imbibe liquid and swell.

7. Consequently, a solid solution may be taken as the limiting case of imbibition, plus adsorption.

Kauffler[1] has developed a formula for calculating the adsorption of a cell:

$$dC = \left(\frac{1}{r_1} + \frac{1}{r_2} + \frac{1}{r_3} + \frac{1}{r_4} \right) \frac{H}{S} \cdot \frac{M}{RT}$$

where dC is the change in concentration produced, r_1 and r_2 the principal radii of curvature inside the cell, r_3 and r_4 the radii of curvature of the exterior of the cell; H, the surface tension, liquid-vapor; M, the molecular weight of the solute; S, the density of the solvent; R, the gas constant, 84,600; and T, the absolute temperature. For a dye absorbed by cellulose cells he obtained very good agreement between calculated and experimental results.

Freundlich,[2] in his recent treatment of adsorption, has very properly referred the explanation of adsorption to the surface tension, *solid-liquid,* rather than to the interface liquid-vapor as Kauffler has done. But although Gibbs'* general equation covers adsorption effects at the liquid-solid surface, we are really at a standstill, because we have no method of measuring the surface tension of a liquid at the boundary of a solid, save the one suggested by Ostwald,[3] based upon the different solubility of fine and coarse grains of the same substance. Even this method is put in doubt by Holty's[4] work on the solubility of cane sugar in pyridine, although Hulett[5] and Duschack[6] and Steinwehr[7] have confirmed Ostwald's generality, that solubility varies slightly

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[1] Zeit. phys. Chem., *43*, 686 (1903).

[2] Zeit. phys. Chem., *57*, 425 (1906).

* $d\sigma = \eta_s\, dt - \Gamma_1\, d\mu_1 - \Gamma_2\, d\mu_2$ where σ is the surface tension; η_s the entropy change due to the concentration of material in the surface layer; t the temperature; Γ_1 the mass of solvent in the surface layer in excess of what would have been there without surface concentration; Γ_2 the same value for the solute, its excess concentration in the surface layer; μ_1 is the chemical potential of the solvent; μ_2 that of the solute.

[3] Zeit. phys. Chem., *34*, 495 (1900).

[4] Jour. Phys. Chem. *9*, 776 (1905).

[5] Zeit. phys. Chem., *37*, 385 (1901).

[6] Zeit. anorg. Chem., *40*, 196 (1904).

[7] Zeit. f. Elektrochem., *12*, 578 (1906). See also Sonstadt, Jour. Chem. Soc., *89-90*, 339 (1906).

with the size of particle of the solid phase in contact with the solution.

In default of a method of measuring this surface tension, solid-liquid, Freundlich has used an empirical formula which describes fairly well the adsorption of a number of solutes from different solvents by various solids. This empirical formula[8] resembles an equation which Freundlich derived from Gibbs' general expression for adsorption. The agreement between the theoretical and empirical equations, and the fact that in general adsorbed substances lower the surface tension, liquid-vapor, of the solvent, leads Freundlich to suggest the probability that these substances likewise lower the vapor pressure, solid-liquid, and are adsorbed as a direct consequence of this lowering.

But Freundlich restricts the application of his distribution formula to dilute solution, and to solutes which are not electrolytes.

Under these conditions, he states that adsorption is independent of the adsorbing solid, the solvent, and the solute used. As these imposed conditions exclude the very chemical systems where we have to deal with pronounced cases of adsorption, it is difficult to gain much, beyond a clearer conception of the factors involved in adsorption, from Freundlich's treatment.[9]

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[8] $\lambda = \frac{v}{m} \cdot \ln\left(\frac{a}{a-x}\right)$, where λ is a constant; V, the volume of solution; *m*, the mass of absorbent; *a*, the total solute in the system; and *x*, the total quantity of solute absorbed.

[9] Ramsden, Zeit. phys. Chem., *47*, 342 (1904), gives a very full discussion of the separation of soluble bodies in the surface layers of solutions, in some instances the solute even separates as a solid. See also, Plauteau, Statique des liquides, *2*, 261-296, Paris, 1873.

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Benson, Jour. Phys. Chem., *7*, 542 (1903).

We are forced to the conclusion that no such simple elimination of the peculiar properties of each individual substance can be made; and, while the fact that a distribution of solute between solid and solution undoubtedly takes place, no general, simple mathematical formula will satisfactorily describe this curve. Each solid, solute, and solvent show marked individual characteristics—attractions; and study along this line of thought seems to offer the path of least resistance.

Poggendorff attributes the first experimental work on capillarity to Leonardo de Vinci, 1452-1519, but a number of investigators worked in this field before it was discovered that capillary phenomena are accompanied by heat effects. Thus, Fontana, in 1777, established the fact that numerous porous bodies retain gases upon their internal surface, but without deducing regularities from his data. Morozzo, Rouppe, and Norden[10] confirmed his observations, in 1800, but Saussure,[11] during 1812 to 1814, was the first to investigate this field extensively. He heated his absorbent material to redness before using, to expel residual gases, and drew the following conclusions: (1) The porous bodies investigated absorb gases; (2) the degree of absorption varies with the form and magnitude of the pores; (3) different substances possess a different absorption capacity; (4) the same substance absorbs different quantities of different gases; (5- easily condensed gases are in general absorbed more easily; (6) absorption decreases as temperature increases; (7) at higher pressure more gas is absorbed than at lower pressure; (8) heat is evolved during the process of absorption.

Pouillet[12] seems to have made the first investigation on record showing the rise in temperature of various powders and porous substances when moistened with a liquid. Unfortunately, he, as well as several investigators following him, neglected to communicate the weight of powder and of liquid used, and their respective specific heats, so we are unable to calculate the calories set free. He gives merely the rise in temperature produced by adding liquid to the material, using water, oil, alcohol, and ethyl acetate, with finely divided metals, metallic oxides, powdered glass, clay, and other substances, including a number of organic

[10] O. Lehmann, Molekularphysik, II part, 83.
[11] Gilbert's Annalen, *47*, 113 (1814).
[12] Ann. Chim. Phys., *20*, 141 (1822); Gilbert's Ann., *73*, 356 (1823).

bodies. Water added to inorganic solids gave a rise of 0.2° to 0.6° C., while with dried organic material the temperature rise was greater, up to 10° C.

Ammon[13] cites the observations of Babo[14] on the rise in temperature experienced by dry soils when subjected to an atmosphere saturated with water vapor. These experiments are qualitative only, but they show the existence of the heat effect due to moistening a powder, that it is positive, and that the temperature rise is greater with soils containing humus than without. Hassenfratz[15] claimed that a substance such as glass after being powdered showed a smaller specific gravity than before, and that the adherence of air to the powder does not account for the phenomenon. He ascribes it to the adhesion of the liquid to the glass, which force increases as the glass-water interface increases. In the case of water, Junk[16] found that above 4° C. there was an increase in temperature, and below 4° a decrease in temperature. This result is attributed to an increase in density at the surface of the powder, which above 4° would tend to increase the temperature of the mass of the liquid, and below 4° would decrease the temperature. Meissner,[17] however, has more recently found an increase in temperature at 0° C. Lagergren[18] has calculated the pressure of the water at the surface of a solid consequent upon the increase in density, and finds a pressure upward of 6,000 atmospheres. Young[19] estimated its value for water at 23,000 atmospheres, while Lord Rayleigh[20] mentions with approval an hypothesis of Dupré, which leads to the value 25,000 atmospheres by a deduction from the dynamical equivalent of the latent heat of evaporation of water. A change in density has also been noted by Spring[21], who found that the amount of water required to fill the spaces of a given mass of sand was greater than would be expected if it were merely a phenomenon of occupying the air spaces. This phenomenon has been ascribed

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[13] Forsch. Agrik.-Physik, *2*, 21 (1879).
[14] Mulder, Chemie der Ackerkrume, Band 3, p. 366.
[15] Gilbert's Ann., *1*, 396 (1799).
[16] Pogg. Ann., *125*, 292 (1865).
[17] Wied. Ann., *29*, 114 (1886).
[18] Bihang. till K. sv. Vet.-Akad., Handl., 24, Afd. II, No. 5 (1898).
[19] Minchin; Hydrostatics and Elementary Hydrokinetics, 311 (1892).
[20] Phil. Mag., (5) *30*, 473 (1890).
[21] Mem. Soc. Geol. Belge, *17*, 13 (1903).

to an increase in the density of the water in the water layer at the surface.

Stellwaag[22] found a marked increase in the temperature on moistening various soils and soil constituents with water and on subjecting them to humid atmospheres. But he has given no data enabling us to calculate the calories liberated during this adsorption, consequently his data have only qualitative value. He concludes: (1) That the rise in temperature which the soil experiences upon addition of water in general is greater the drier the soil, the finer its grains, and the lower the prevailing temperature; (2) that the rise of soil temperature on addition of water to a perfectly dry soil is very considerable (8.33° C. for a calcium carbonate sand rich in humus; 6.6° C. for ferric hydroxide; 5.57° C. for a loam soil); (3) when water vapor is adsorbed by soil constituents, a temperature rise is observed as follows: Quartz sand, 0.00 to 0.25 mm. diameter, 0.88°; quartz powder, 1.08°; precipitated calcium carbonate, 1.47°; kaolin, 2.63°; ferric hydroxide, 9.30°; peat, 12.25° C. (4) The higher the temperature of the air saturated with water vapor, the finer the soil particles, and the dryer the soil, the greater is the rise in temperature due to adsorption. (5) That the temperature rise due to adsorption of dry carbon dioxide by dry soil constituents is inconsiderable, with the exception of ferric hydroxide, in which case the rise is 6.9° C., while the moist gas is adsorbed with a much greater temperature increase. (6) Dry soil constituents adsorb dry ammonia and experience a considerable temperature rise; quartz powder, 0.80°; precipitated calcium carbonate, 0.80°; kaolin, 2.05°; ferric hydroxide, 18.05°; peat, 28.3° C. Moist ammonia shows less temperature rise; for ferric hydroxide and for peat it is respectively 14.1° and 23.80° C.

Martini[23] gives 13.73 calories as the heat evolved on wetting one gram of quartz powder with water. A mechanical analysis of the powder is not given. Similarly, charcoal evolved 14.45 calories per gram when placed in water. Ercolini[24] finds slightly different values, 13.23 calories for quartz, and 14.23 calories for charcoal. Martini[25] found each liquid has its own heat of

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[22] Forsch. Agrik.-Physik, *5*, 211 (1882).

[23] Atti del R. Istituto Veneto, (7) *9*, 958 (1897).

[24] Nuovo Cimento, (4) 9, 110 (1899).

[25] Atti del R. Istituto Veneto, (7) *8*, 510 (1896).

wetting. Thus, with C. P. granulated animal charcoal at 17° to 18° C., water showed a rise in temperature of 15.58°; absolute ethyl alcohol, 17.47°; ethyl ether, 17.50°; ethyl acetate, 18.94°; benzene, 17.60°; carbon disulphide, 20.60°. It is interesting to note, too, that benzene with impure charcoal gave no rise in temperature, and that amyl alcohol showed this same indifferent action, evolving no heat. Absolute alcohol caused a rise of 5.55° only, whereas less pure alcohol showed 10.30° rise. These results are not given in calories.

Linebarger,[26] using the same sample of quartz powder with which Martini worked, found 13.80 calories evolved per gram, when placed in water, 11.21 and -0.88 calories for nitrobenzene; 9.61 and 7.55 calories for toluene; 4.09 calories for benzene; 11.84 and 12.46 calories for pyridine. The granules of this powder had an average diameter of 0.0005 cm. Using another sample, with average diameter of grain, 0.00096, Linebarger found that practically half the quantity of heat given above for each liquid was evolved on wetting. Benzene gave the same quantity of heat with fine and with coarse quartz powder, but as this experiment stands alone in the literature, it should be carefully confirmed before laying stress upon it. Linebarger found, in common with previous investigators, that the relative amount of liquid does not influence the heat effect. A certain minimum quantity of liquid is necessary to produce the maximum heat change, but any excess of that amount has no perceptible influence. The heat effect per unit mass of the powder is the same for the same liquid at the same temperature, provided this minimum amount be present.

An attempt to discriminate between moisture held by a powder as "hygroscopic moisture," and that in the capillary spaces, meets with difficulty.[27] We have no sharp experimental method of ascertaining what fraction of the water is retained on the surface of the grains. This is especially so as an even distribution of moisture throughout the powder is hard to secure, and failing of this, the powder is balled together and holds part of the liquid in its capillary spaces between the grains.

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[26] Phys. Rev., *13*, 48 (1901).

[27] Soyaka, Forsch. Agrik.-Physik, *8*, 1 (1885).
Whitney, Agricultural Science, *3*, 199 (1889).
Katao, Über die Wasser bewegung in Boden, Bull. College of Agriculture, Imperial University of Japan, Vol. 3, No. 1 (1897).
Briggs, Bull. No. 10, U. S. Dept. of Agr., Division of Soils (1897).

Still, the experiments of Parks[28] indicate that the quantity of water adsorbed by a powder from water vapor is very nearly the same as the quantity of water held on the surface of the grains when the powder is immersed in liquid water. He has shown that a silica powder saturated with water vapor gives off no measurable heat when brought into contact with liquid water, whereas the dry silica liberates a definite quantity of heat per square centimeter of surface; and this heat evolution decreases in a perfectly regular manner, as the silica powder contains more and more adsorbed water vapor.

The heat which water vapor liberates when it condenses upon the surface of the silica grains is returned to the liquid water (which is in the vessel with the silica to maintain the air space saturated wth water vapor), as that evaporates to take the place of the water vapor which the silica has adsorbed. In the end, therefore, the same quantity of water is adsorbed and the same quantity of heat liberated when the silica is in contact with water vapor as when it is placed under liquid water.

In another paper,[29] Parks formulates a law: "When silica sand or glass is brought in contact with water at approximately constant temperature, the heat evolved is proportional to the area of the surface exposed by the solid, and the amount of heat developed per square centimeter is approximately 0.00105 calorie when the temperature is near 7° C." And for a range of 17 degrees, from 7° C. to 24.3° C., this heat evolution increases 0.000,003,5 calorie per square centimeter of surface for each degree increase in temperature. It has been suggested that this law of Parks' may be used to ascertain the area of powder or a soil per gram, by determining experimentally the heat evolved when the powder is placed in water, and dividing this quantity of heat by the calories which one square centimeter of surface liberates when wetted. But here again we meet the same difficulty which confronted Kayser[30] in his attempt to determine the area of the surface presented by the grains of powder, by measuring the quantity of water adsorbed by the powder, and then dividing this weight of water by the number of grams of water absorbed upon a unit surface of standard material. He failed to find a

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[28] Phil. Mag., (6) 5, 521 (1903).
[29] Phil. Mag., (6) *4*, 247 (1902).
[30] Wied. Ann., *24*, 450 (1885).

standard material. Each surface tried showed a different degree of adsorption. And the researches quoted above show that each soil constituent has its own heat effect when moistened; consequently, an attempt to measure the area of a soil in this manner is not promising.

In Linebarger's experiments,[31] the heat evolved compared to the surface of silica exposed is greater than that shown by Parks. But, in considering this apparent clash of results, one must bear in mind that Linebarger has measured the heat effect of the same solid in different liquids, and finds the ratio of the different heat effects for coarse and fine powder the same in different solvents. This is very strong evidence, indeed, that the heat evolved is proportional to the surface. The error involved in calculating the effective area of a powder is enormous. Parks' values involve the area as calculated from microscopic measurement of the granules. Linebarger's ratio is absolute, since he takes merely average samples of each grade of powder, without attempting to evaluate the area, and uses these two samples with each liquid.

Masson[32] has shown that the heat evolved when cotton absorbs water vapor is for practical purposes directly proportional to the quantity of moisture absorbed, and is very nearly the same as the latent heat of vaporization. He finds the absorption by cotton to be much greater than is warranted by its area as compared with similar experiments using glass wool, and suggests, as an explanation, that the water adsorbed penetrates into the cotton fiber as a solid solution. The thermal effect dealt with here is evidently different from that studied by Parks.[33]

[31] Phys. Rev., *13*, 48 (1901). See also
Cantoni, Rend. del R. Istituto Lombardo, *8*, 135 (1866).
Martini, Atti del R. Istituto Veneto, (7) *8*, 502 (1896); (7) *9*, 727 (1897); (8) *2*, 615 (1900).
Tait, Proc. Roy. Soc. Edinb., *11*, 51 (1880-81); *11*, 813 (1881-82).
Marshall Smith and Omond, Ibid., *11*, 626 (1881-82).
Amagat, Compt. rend., *116*, 946 (1893).
Lussana, Nuovo Cim., (4) ii, 233 (1895).
Lagergren, Köngl. Vet. Akad. B., *24*, Afd. ii, Stockholm (1899).
Tate, Phil. Mag., (4) *20*, 508 (1860).
Melsens, Mem. Acad. Belg., *23* (1873); Ann. chim. Phys., (5) *3*, 522 (1874).
Chappuis, Wied. Ann., *19*, 21 (1883).
Wiedeman and Lüdeking, Wied. Ann., *25*, 145 (1885).
Gore, Phil. Mag., *37*, 306 (1894); Birm. Phil. Soc. Proc., *9*, part 1 (1893).
Ercolini, Nuovo Cim., (4) *9*, 110 (1899).
Bellati, Atti del R. Istituto Veneto, (8) *2*, 931 (1900).
Fitzgerald, Nature, *49*, 293, 316 (1894).
Weber, Pogg. Ann., *154*, 367 (1875).
Barus, Phil. Mag., (6) *4*, 24, 262 (1902).
Magnus, Phil. Mag., (4) *6*, 336 (1853).

[32] Proc. Roy. Soc. London, *74*, 249 (1904-05).

[33] *Loc. cit.*.

Rodewald[34] has studied quantitatively the energy changes of starch as it absorbs water. One specimen evolved 24.02 calories per gram of starch; another, 19.4 calories. He finds that the greatest available effect in the passage of heat into work which can be reached in the swelling of starch is 11.4 per cent. of the total heat effect, 24.02 calories. This result is based upon measurements of volume change during swelling. The average pressure between the ultramicroscopic cells of starch is calculated as 2,137 atmospheres, while very near to a cell wall the pressure would be much greater. Comparing this value with those of Dupré (25,000 atmospheres) and Young (23,000 atmospheres) and Lagergren (6,000 atmospheres), it seems probable that in the swelling of starch the imbibition effect predominates over the adsorption.

Knop,[35] Kayser,[36] Ammon,[37] and Dobeneck[38] have shown that at higher temperatures absorption is very considerably decreased. Bunsen[39] found that a temperature of 503° C. was required to remove adsorbed water from glass. At 23° C. a layer of moisture as thick as 1.0×10^{-5} mm. may be retained on glass over P_2O_5. Day and Allen[40] have confirmed this result. They state that a low red heat, 600° to 800° C., is required to remove adsorbed water from minerals.

T. W. Richards,[41] and Rogers, too, have shown that zinc oxide derived from the nitrate, even when heated to very high temperatures, retains nitrogen and oxygen. Morse and Arbuckle[42] confirmed these results, but found no evidence supporting Richards' and Rogers' conclusion, that the absorbed oxygen escapes more readily than the nitrogen. The zinc oxide was heated by Morse and Arbuckle to a temperature sufficient to melt cast steel and still retained per gram of oxide some 0.3 cc. of gas whose composition varied, the nitrogen between 64.32 and 68.18 per cent.; and the oxygen correspondingly, while the total volume of occluded gas was very constant for eight different experiments.

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[34] "Researches on the Swelling of Starch," Lipsius & Fischer, Leipzig, 1896.

[35] Cited by Johnson, How Crops Feed, pp. 161-162.

[36] Ann. d. Physik, *14*, 450 (1885).

[37] Forsch, Agrik.-Physik, *2*, 36 (1879).

[38] Ibid., *15*, 163 (1892).

[39] Ann. d. Physik (N. F.), *24*, 321 (1885).

[40] Pub. Carnegie Institution of Washington, No. 31, pp. 56; Am. Jour. Sci., (4) *19*, 93 (1905).

[41] Proc. Am. Acad. Arts and Sci., *28*, 200 (1893).

[42] Am. Chem. Jour., *20*, 200 (1898).

Saussure first observed that a powder gives out heat when it absorbs a vapor. This was naturally attributed to the latent heat made available by condensation of the vapor, but Favre[43] found this heat due to absorption much in excess of the latent heat for three different gases, so this assumption had to be abandoned.

Dewar[44] has found that charcoal and lamp-black are nearly equal in absorbing power for gases at the temperature of liquid air, and that graphite is only one-fourth as good an absorbent. As to the heat developed by absorption, in general it is greatly in excess of the latent heat of vaporization. Thus, hydrogen, whose latent heat is 120 gram-calories at its boiling point, gives off six times that amount of heat when absorbed by charcoal at the boiling point of air. Similarly, oxygen gas when absorbed liberates twice the heat due to liquefaction.

The behavior of helium toward charcoal is interesting. While it resembles other gases in showing increased absorption at the temperature of liquid air, the absolute amount occluded is about one-tenth that of the other gases at the same temperature, and the quantity of heat evolved is in even a smaller ratio. But helium is being absorbed at a temperature some 15 times higher than its boiling point (about 6° absolute), while in the case of hydrogen this is only four and one-half times its boiling point (20° absolute). To make a fair comparison, we should take hydrogen at fifteen times its boiling point, which would bring us up to some 27° C.—that is, the helium absorption at —185° C. should be compared with the hydrogen absorption at 0° C. The inference, then, is that if we had the absorption of helium at 25° to 30° absolute, we should find it showing a still more remarkable condensation than hydrogen at 90° absolute (—183° C.).

It is sufficient to note here the mass of experimental work which has been carried out upon the absorption and retention of gases by metals.[45] Especially interesting are the points made by M. Thoma:[46]

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[43] Lehmann, Molecular Physik, II, p. 85.

[44] Chem. News, *94*, 174 (1906); Proc. Roy. Soc., *74*, 130 (1904).

[45] Cited by E. Bose, Zeit, phys. Chem., *34*, 738 (1900).
Schönbein, Pogg. Ann., *43*, 89 (1838).
Matteuci, Compt. rend., *7*, 741 (1838).
Grove, Phil. Mag., (3) *14*, 129 (1839); Pogg. Ann., *57*, (1842).
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Buff, Ann. Chem. Pharm., *41*, 136 (1842); Arch de l'Elect., II, *222* (1842).
Grove, Phil. Transact., *133*, 91 (1843).
Matteuci, Compt. rend., *16*, 846 (1843).
Schönbein, Pogg. Ann., *58*, 361 (1843); Phil. Mag., *22*, 165 (1843).
Peltier, Bibl. univ., *18*, 186 (1843).
Poggendorff, Pogg. Ann., *58*, 207 (1843).
Henrici, Pogg. Ann., *58*, 384 (1843).
De la Rive, Arch. de l'Elect., III, 525 (1843).
Smee, Phil. Mag., (3) *25*, 435 (1844).
Schönbein, Pogg. Ann., *62*, 220 (1844).
Poggendorff, Pogg. Ann., *61*, 598 (1844).
Grove, Phil. Mag., (3) *24*, 286 (1844).
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E. Becquerel, Ann. chim. Phys., (3) *37*, 385 (1853).
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Helmholtz, Ber. der Berl. Akad. 1876, 217; Pogg. Ann., *159*, 416 (1876); Gesammelte Abhandl., *1*, 835.
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Krouchkoll, Compt. rend., *45*, 177 (1882).
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Hopfner, Zeit. anorg. Chem., *20*, 419 (1899).
Bose, Zeit. phys. Chem., *34*, 738 (1900).
Lewis, G. N., Ibid., *55*, 485 (1906).

[46] Zeit. phys. Chem., 3, 69 (1889).

(1) The increase in volume of palladium, upon which hydrogen is liberated electrolytically, takes place equally in all directions. (2) The contraction where oxygen is liberated upon the palladium becomes less with the number of the treatments, but shows, nevertheless, no definite regularity. (3) Palladium can retain only a definite quantity of hydrogen firmly fixed; any excess of this amount absorbed it again gives off spontaneously (pressure and temperature, of course, determine this limit). (4) Below this saturation limit, the expansion of the palladium, as well as that of the alloys of palladium and platinum, are proportional to the mass of hydrogen absorbed. (5) The absorption of hydrogen by palladium, and by the alloys, above the "saturation limit" takes place likewise with expansion, and the spontaneous loss of this extra absorbed hydrogen is accompanied by a contraction of the palladium. (6) The expansion for the supersaturation is equal to the contraction on spontaneous loss of excess hydrogen. (7) Each current density used to liberate hydrogen electrolytically upon the metals corresponds to a definite degree of supersaturation which cannot be exceeded by long-continued electrolysis. (8) Most probably there is a stationary condition for each degree of supersaturation reached at a definite current density, so that in one second just as much hydrogen penetrates into the cathode as is set free. (9) Above the saturation limit the volume of the palladium increases much faster for equal hydrogen absorption than below the saturation limit. On this account the hydrogen exists in the palladium in a much less dense condition above the saturation limit than below it. (10) The hydrogen distributes itself in the palladium wire during a duration of electrolysis of a half-hour to a point four to five millimeters distant from the point where the palladium wire enters the electrolyte. (11) In the supersaturated condition, palladium shows, as well as its platinum alloys, a far higher hydrogen polarization than in the saturated condition. (12) Iron in similar manner may be supersaturated with hydrogen, and it may likewise lose hydrogen spontaneously. (13) This supersaturation always occurs when iron comes in touch with "dissociated" (electrolytic or "nascent") hydrogen, whether produced in an electrolytic cell or by action of acids upon iron, but not when the iron is placed in free hydrogen gas. (14)

Likewise, in the case of iron, each current density corresponds to a definite degree of supersaturation of iron with hydrogen. (15) The hydrogen gas spontaneously evolved from supersaturated iron is proportional to the surface of the iron.

Hoitsema[47] found that increase of pressure occasioned increase in the quantity of hydrogen absorbed by palladium, but the relation of pressure to mass of gas absorbed is not a simple mathematical expression.

Recently, Fischer[48] has measured the change in electrical resistance of palladium wire produced by hydrogen absorbed from the free gas. The resistance is greatly increased, even by the first quantities of hydrogen absorbed, the curve, resistance-volume, rising steeply. The rate of increase in resistance gradually decreases until about 30 volumes of hydrogen to one of palladium have been absorbed; from this point on up to 950 volumes of hydrogen in palladium the resistance rises steadily in direct (linear) proportion to the volume of the hydrogen absorbed. At 950 volumes hydrogen, a sudden change in the resistance-volume curve takes place, the resistance rising less steadily with the volume of hydrogen absorbed. A palladium wire contains in saturated condition about 1,000 volumes of absorbed hydrogen. (2) Supersaturation with hydrogen produces no further change in the resistance, and hydrogen thus retained is freely given off without affecting the resistance. (3) The resistance of a palladium wire rises to 1.69 times its original value through the absorption of hydrogen, and this change is due solely to the hydrogen occluded. (4) The linear expansion of the metal is directly proportional to the mass of hydrogen absorbed, that is, 0.000,025,39 cm. per cm. for each volume of hydrogen up to the point of saturation; supersaturation with hydrogen causes a proportionate increase in length. (5) Withdrawal of the hydrogen, either by spontaneous evaporation or by treatment with oxygen, leaves the wire shorter than it was originally, but its resistance is just the same as before the hydrogen was absorbed.[49]

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[47] Zeit. phys. Chem., *17*, 1 (1895). See also Burgess and Hambuechen, Trans. Am. Electrochem. Soc., *5*, 204 (1904).

[48] Ann. d. Physik, (4) *20*, 503 (1906).

[49] Consult W. P. Grahm, Pogg. Ann., *136*, 325 (1869); C. G. Knott, Proc. Roy. Soc. Edinb., *12*, 181 (1884); Trans. Roy. Soc., Edinb., *33*, 171 (1888); A. A. Krakan, Zeit. phys. Chem., *17*, 689 (1895).

Thus it is clear that occlusion of gases by metals is a complex phenomenon, involving surface, diffusion of gas in the metal, specific attraction of gas and metal for each other, and in some cases a compound of metal with gas may even persist over a considerable range of pressure and temperature. In connection with the use of metallic electrodes for electrolysis and for both primary and secondary batteries, the retention of gases by metals has received much attention.

Regarding the absorption effect shown by innumerable contact reactions, the field is so wide that it can receive only mention here. Of special interest is the recent work by A. A. Baikoff.[50] Using a Le Chatelier pyrometer, he showed (1) that solid bodies, such as platinum, quartz, and porcelain, heated in the same flame are raised to temperatures which differ from each other and from that of the flame. (2) The temperature which a solid takes depends upon the catalytic properties of the body and upon the ratio of its surface to its volume. (3) Consequently, the true temperature of a flame is up to the present time an undetermined magnitude. (4) A porcelain crucible and a platinum crucible of the same size, heated in the same flame, may differ in temperature by 400° C.

Thoma[51] has shown that iron wires 1 to 2 mm. in diameter used as cathodes and hydrogen liberated upon them, when cut up and placed in a microscope field under water, evolve gas bubbles from the cross section, thus clearly showing the penetration of the hydrogen gas into the metal. Carbon electrodes boiled out with water and similarly treated did not evolve hydrogen. Thoma suggests that the carbon in iron may increase its power of retaining hydrogen; he found that iron rich in carbon evolves very little gas under water. Zinc wire appears not to absorb hydrogen, even electrolytic hydrogen, but more recently W. Ternent Cooke[52] has shown that zinc has a density 12 per cent. higher in argon than in nitrogen, but this effect is not marked in helium; cadmium has a density 12.4 per cent. higher in helium than in hydrogen, while in argon no such change was observed; arsenic and sulphur show no increase in density in

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[50] Jour. Soc. phys. Chim., R., *37*, Fas. 2, 156 (1905); abstr., Bull. Soc. Chim., *35*, 1202 (1906).

[51] *Loc. cit.*

[52] Zeit. phys. Chem., *55*, 546 (1906).

helium or argon, while for selenium the increase is very slight in both these gases. The metals gold, silver, copper, tin and lead, and drawn nickel wire did not evolve hydrogen when used as cathode, cut up, and placed under water, while commercial nickel and aluminum behave like iron, giving off hydrogen when immersed. Raoult,[53] in 1869, made the same observation for nickel. Soddy[54] recommends metallic calcium as an absorbent for all the common gases at temperatures between 700° and 800° C., for pressures not above a few millimeters of mercury. By this method vacua are obtained, through which the electric discharge cannot be forced. Barium and strontium behave similarly, but are less suited for practical use.

Berthelot[55] finds that nitrogen is absorbed by paper under the influence of radium. He placed 1.424 gr. white blotting paper in a tube containing 29.1 cc. air and 0.02 gr. radium chloride, sealed off the tube, surrounded it on the outside with a double layer of gray paper, and left it eleven months in a cupboard. At the end of this period the tube contained 17 cc. of gas, 15.5 cc. nitrogen, and 1.5 cc. carbon dioxide; thus, 7.6 cc. nitrogen and 6 cc. oxygen had disappeared, and it was found that both these gases had been fixed by the paper, which was slightly yellowed, especially near the radium salt. The paper jacket about the tube was unaltered, showing that this effect is produced by rays from the radium, which do not penetrate glass.

Rutherford[56] is investigating the absorption of radium emanation by charcoals, especially that from cocoanut, while Bunzel's[57] experiments show that wood charcoal absorbs radium emanation to a high degree.

The foregoing experiments may be summarized as follows:

(1) Porous bodies absorb gases, even those most inert chemically. Plane surfaces of solids show the same power of retaining gases.

(2) The degree of absorption varies with the form and size of the pores; in general, the greater the surface the greater the absorption.

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[53] Compt. rend., 1869, p. 829. See also Bellati and Luscana. Atti d. R. Istituto. Veneto, *6*, 6 (1888).

[54] Chem. News, *95*, 13 and 25 (1907).

[55] Compt. rend., *143*, 149 (1906).

[56] Nature, *74*, 639 (1906).

[57] Wien. Sitz. Ber. Math. Natur W. Kl., Bd. 114, Abt. iia, pp. 21-31 (1906).

(3) Different substances possess a different absorption capacity.

(4) The same substance absorbs different quantities of different gases.

(5) Solids exercise a selective absorption toward mixed gases; mixtures of solids absorb a gas additively.

(6) Easily condensed gases are in general absorbed more easily.

(7) Heat is evolved during the process of absorption, but this heat is greatly in excess of that given out by the condensation of the vapor to liquid.

(8) At higher temperatures, absorption is very considerably decreased.

(9) Absorbed gases are held with remarkable tenacity; hygroscopic water is completely removed from glass and mineral surfaces only at temperatures ranging from 500° C. to 800° C.

(10) Thus the water is present under its vapor pressure, which at these high temperatures amounts to hundreds of atmospheres, and it is seen why pressure changes within one atmosphere are of little effect upon the absorption while the initial layer is being adsorped.

(11) The portions of gas absorbed later are held less strongly and are under lower vapor pressure; and for them the quantity of gas absorbed increases with the vapor pressure, but not according to a simple mathematical formula, although several have been proposed.

(12) The adsorption of gases upon solids is not due to the solution of gas in a moisture layer on the solid, as is shown by the adsorption of gas by bodies which have been heated to redness and cooled in a vacuum.

(13) The absorption of gases by solids has recently been shown to render uncertain all of the attempts to measure the temperature of a flame by immersing in it a solid and determining the temperature of the solid. Porcelain and platinum may differ from each other by 400° C. while in the same flame.

(14) The heat evolved upon wetting a powder with liquid is not influenced by the relative quantity of liquid added beyond the certain minimum volume of liquid required to produce the maximum heat effect. The finer the powder, the greater the heat

effect for the same solvent. The heat evolved is different for the same substance wet with different liquids. Soils show a temperature rise upon addition of water of 5° to 8° C.

(15) A powder in equilibrium with vapor at a given temperature and pressure can retain practically as much condensed vapor adsorbed on its surface as when kept below the liquid water at the same temperature and pressure.

(16) In many instances a substance, such as starch, imbibes a liquid and swells. Here we have both imbibition and adsorption, and the heat evolved is, as we should expect, greater than for simple imbibition, and less than that observed where adsorption is the main effect.

(17) When a gas is absorbed by a metal, many interesting physical changes in the metal may be effected. Its volume, hardness, elasticity, electrical conductivity, and single potential and rate of solution in various solvent liquids are changed. The absorption of a gas, too, may depend upon its condition—that is to say, the energy it possesses. For example, free hydrogen gas is very slightly absorbed by iron and some other metals, but hydrogen freshly liberated from combination either by electrolysis or by action of metal upon acid is very strongly absorbed by the iron. Palladium, on the other hand, absorbs free hydrogen with great avidity.

(18) Radium gives off radiant energy which causes paper to absorb nitrogen and oxygen.

(19) Radium emanation is absorbed by charcoal.

Bureau of Soils,
U. S. Department of Agriculture,
Washington, D. C.

DISCUSSION.

PROF. W. D. BANCROFT: I should doubt very much whether it was possible to pass without change of treatment from the adsorption phenomena, or the phenomena observed in the colloids, to the case of solid solutions. In the case of solid solutions, we know experimentally that we can neglect the surface tension effects; in the other cases, we know experimentally that we cannot neglect the surface tension effects, that surface tension appears as an important variable; and while, of course, one can say that you can consider, for instance, a solid bar of metal as made up of an infinite number of small particles, each one of which has a large surface, still we all know experimentally that metallic powder in the form of a bar is not the same thing as a cast bar; and I think the same thing applies to the relation between colloids and solid solutions.

Mr. H. E. Patten: I took account of that when I suggested the application of this viewpoint to systems where we have definite physical evidence that the solid phase is not homogeneous, but rather, shows a cellular structure. For example, the colloidal silicic acid gel becomes opalescent at a certain stage in its dehydration, thus giving clear indication of a vast internal surface. If we wish to assume such a cellular structure for a solid solution, we can certainly use the general knowledge at our command concerning adsorption to explain the distribution of a solute or radical between the solid solution and the liquid solution in contact with it. In doing this, we necessarily pass from the region of measurable physical evidence over to the hypothetical region of molecular dimensions. We can, of course, treat of solid solutions and map the condition ranges which bound their fields of existence entirely without reference to surface tension. But having done this, it is certainly advantageous to connect, in thought at least, these experimentally determined and mapped properties with the properties of the same substances when spread upon a great surface.

Prof. Bancroft: That may help in clearing up Mr. Patten's views, but I object very strongly to appearing on record as having said that a solid solution has anything whatsoever to do with molecular dimensions. I based what I said solely on the experimental facts with regard to solid solutions, and I don't care whether you have any dimensions at all.

Prof. J. W. Richards: I notice, in connection with paragraph 13, that the adsorption of gases by solids has recently been shown to render the attempts to measure high temperatures inaccurate.

I have always supposed that the difference between the temperatures of two solids immersed in the same flame was due to the effect of the surface of the solid upon the combination of the gases in the flame. There is, as you might say, a catalytic effect in causing more or less complete combination of the gases in the flame, and also a difference in power of radiating heat possessed by the solids in the flame, that changes their temperatures. I would like to ask if those views have been shown to be proved or upset by the adsorption phenomena?

Mr. Patten: I have quoted the work of Baikoff and his views, and summarized them here. That is all.

Prof. Richards: It was not the subject of your own investigations?

Mr. Patten: No.

APPENDIX

APPENDIX.

A BRIEF DESCRIPTION OF WORKING MODELS OF ELECTRIC FURNACES.

Exhibited to the Members of the American Electrochemical Society, Friday, May 3, 1907 at the Lardner's Point Station of the Philadelphia Electric Company.

(From a Pamphlet Distributed by the Company.)

Colby Induction Furnace.

The induction furnace shown is manufactured by the Induction Furnace Co. of America under the patents of Edward A. Colby. The fundamental patents covering this furnace are numbered 428,378 and 428,379, issued May 20, 1890, applications bearing date of September 7, 1887.

This furnace is of 131 K. V. A. capacity and the annular crucible has a working capacity of about 190 pounds of steel.

The primary, consisting of 28 turns of copper tube, ⅜ inch inside and ⅝ outside diameter, is cooled by water circulation and is calculated to utilize 541 amperes at 240 volts at a maximum.

The secondary consists of an annular one-piece crucible and its contents. This crucible is 14⅞ inches inside and 24¼ inches outside diameter, 8 inches in height. The trough is 6⅜ inches deep, 2 7-16 inches wide at top, and 2 inches at the bottom. The current in this trough is, at a maximum, 15,148 amperes at 8.57 volts.

This furnace was put in operation about one year ago by Henry Disston's Sons, Inc., for the manufacture of high-grade crucible and special steels.

Experience has shown that with this furnace a 90-pound ingot can be poured practically every hour, and that the expenditure of electrical energy amounts to from 25 to 34 K. W. hours per ingot according to the carbon contents of the steel.

Kryptol Furnace.

The first melting furnace shown is a convenient adaptation of the use of Kryptol for use with crucibles at moderate temperatures.

Plates of Acheson graphite are placed at each end of a cham-

ber built up of refractory materials and the crucibles are plunged in Kryptol, which is packed around them.

This furnace consumes about 7 K. W., and, by inserting resistance in the circuit, the temperature may be readily controlled.

Arc Furnace.

The arc furnace, with two electrodes, is something on the order of the Heroult furnace in use at La Praz. The arcs are produced between the electrodes and the slag on top of the metal. From 300 to 500 amperes at from 35 to 40 volts are used at each electrode, making the total current consumption in the furnace from 21 to 40 Kilowatts.

This furnace has been used experimentally in reducing iron ores.

Arc and Resistance Furnace.

The single electrode arc furnace is of the type used by Siemens, Menges, Willson, Heroult and other investigators. In this case the crucible and its contents are connected with one side of the circuit and the movable electrode the other. The current used in this model has been from 300 to 500 amperes at 35 to 50 volts, a total capacity of from 10.5 to 25 Kilowatts. It has been used principally in the production of carbides of various metals.

Resistance Furnace.

This furnace is of a type controlled jointly by the Allgemeine Elektricitäts Gesellschaft of Berlin and the General Electric Co. in this country.

It is intended for use in hardening and annealing, and for this purpose is meeting with considerable success in European countries.

The terminal plates, or electrodes, are of wrought iron. The bath consists of fused chloride of barium for temperatures above 1000° C. For lower temperatures a mixture of chlorides of barium and calcium is used.

It takes about half an hour to heat up thoroughly, and the current consumption ranges from 8.5 to 12 Kilowatts.

A wide range of temperatures is possible by adjusting the voltage.

Since the current density in the molten bath is practically uniform, the temperature within the bath, except in a thin layer at the upper surface, is found to be very uniform.

Articles requiring to be heated to a high temperature, such as the high speed steels, can be immersed in the bath, without oxidation or other chemical action, and be quickly brought up to the required temperature.

Miscellaneous.

Upon the bench may be seen a device for heating a combustion tube by the use of Kryptol. This consists of an inner and outer containing tube with the Kryptol powder packed between them. Contact is made by terminal blocks of Acheson graphite. A wide range of temperatures may be attained by the use of supplementary resistance control.

Two small arc furnaces of the Moissan type are shown in operation.

The small induction furnace is of interest only as showing the principle of construction of this type of apparatus.

ELECTROLYTIC PROCESSES FOR REFINING GOLD AND SILVER.

Seen at the United States Mint at Philadelphia, Visited by the Society Saturday, May 4, 1907.

(NOTES BY CARL HERING.)

The electrolytic processes for refining gold and silver at the Mint have replaced the former chemical processes entirely. The reasons are that greater purity of the gold and silver is obtained and the cost of the process is less; incidentally, also, the platinum is recovered, which formerly was lost.

In general, the process is that the crude bullion, made to contain about 30 per cent. gold and 70 per cent. silver, is first electrolized to obtain the pure silver, and the residues, consisting almost entirely of gold, are then electrolized to obtain pure gold. The other impurities either go into solution or into the slimes and are treated separately, the only one of value being the platinum.

Silver Process. The anodes are made to contain about 3 parts of gold and 7 of silver. The solution contains 3 per cent. of silver nitrate and 1.5 nitric acid. The current density is 0.05 ampere per square inch, which is quite low. The silver and many other metals are dissolved, but only the silver is deposited, in a very pure state. The gold remains in a coherent black porous mass, resembling compressed lamp black. An important improvement made by Dr. Tuttle, the melter and refiner of the Mint, consists in the addition of gelatine to the solution, the result of which is that the silver crystals become adherent and may be taken out by lifting out the cathodes and melting down. This greatly simplifies the removal of the crystals of silver. For other details, see Electrochemical and Metallurgical Industry, August, 1906, p. 306.

Gold Process. The Wohlwill process is the one used. The anodes are moderately pure gold; the process is used only for obtaining the very purest gold. The chief feature of the process is that the solution is chloride of gold strongly acidulated with hydrochloric acid; under these circumstances, the gold is dissolved at the anodes in electrochemical proportions and the solution therefore is not depleted. The solution is heated to 50-55° C.

The current density is very high, being nearly one ampere per square inch; hence, the plant is small. This is of importance, as the solution is worth about $1,500 per gallon. The gold comes out very pure, as adherent crystals. By this method, the platinum formerly lost in the chemical process, is now recovered. For further information, see Electrochemical and Metallurgical Industry, January, 1903, p. 157. Also an article by Wohlwill, vol. II, p. 221, of the same journal.

A feature of interest from the commercial point of view is that, unlike in an industrial establishment for such refining, the Government does not have to consider the question of the interest on the value of the gold during the process of refinement, as the Government issues paper notes when the bullion is purchased. The question of this interest, which, in a commercial establishment would be very large, therefore does not enter. Another feature of interest is that as the Government refines gold for a very slight fee only, and as there is no limit to the amount of gold which the Government will take, there is no inducement to any commercial industry to refine gold in this country.

ELECTRICAL PLANT FOR THE PURIFICATION OF WATER BY OZONE.

Shown to the Society by the United Water Improvement Company of Philadelphia, May 2, 1907.

(FROM A PAMPHLET PREPARED BY THE COMPANY.)

A plant for demonstrating the efficiency of ozone in the purification of public water supplies, which formed the subject of a pamphlet by Mr. James Howard Bridge, has been completed on the banks of the lower Schuylkill, in West Philadelphia, and is daily purifying large quantities of water taken from this foul stream. The process has been subjected to an exhaustive series of tests, extending over many weeks, by Dr. Rivas, official bacteriologist of the City of Philadelphia, supplemented by independent tests by Drs. Jackson and Hale, city bacteriologists of Greater New York. The signed records of Dr. Rivas show that the raw water of the Schuylkill, at the point where it is taken from the river, is nothing but diluted sewage. It contains as high as 2,500,000 bacteria per cubic centimeter, which is twenty drops; after a rough straining, to remove the coarser particles of suspended matter, the water contains from 253,000 to 700,000 bacteria; after ozonization it contains from 5 to 55, the average being 25. The 25 bacteria which are left are of the harmless varieties, mainly the hay bacillus, which has no effect whatever on the human organism. The bacillus coli, always found in sewage, always the companion of the typhoid fever germ, a sure indication of organic pollution in water, and very abundant in raw Schuylkill water, is found to have been entirely destroyed by ozonization. The offensive odor of the water is also destroyed, and its discoloration removed. In brief, the tests have demonstrated that the foulest water can be rendered absolutely free from disease-breeding germs, made bright and sparkling and free from color and odor, and rendered as palatable as the finest spring water. The following is an abstract of the reports of the scientists named above:

Dr. Rivas.

Date	Sample	Bacteria Before Ozonization (includ'g disease germs).	 After Ozonization (no disease germs)	Organic Matter in Solution. Before	 After
May 15. 1905	1	720,000	16	15.21	7.7
May 15. 1905	2	253,000	37	13.33	8.89
May 18, 1905	1	500,000	55	11.96	7.51
May 18, 1905	2	500,000	38	19.92	7.11
May 19, 1905	1	700,000	5	10.07	6.52
May 19, 1905	2	700,000	0	12.64	6.72
Average		562,100	25		

Drs. Jackson and Hale.

Date	Sample	Bacteria Before	Bacteria After	B. Coli after Ozone
May 19, 1905	1	665,000	15	0
May 19, 1905	2	648,000	13	0

More recent tests confirm the foregoing. They also establish costs of operation. [See last column.] A kilowatt-hour costs one-fifth to one-half cent; so that at the higher figure, ozonization costs for electricity less than an average of one dollar per million gallons treated. Here are all the figures for one week's run:

Date	Quantity of Water gals. per hr.	Bacteria Before Ozonization	 After Ozonization	Electrical Expenditure K. W. hr.	Rate per million gals. in K. W. hrs.
Dec. 14, 1905	31,200	1.500	2	6.1	196
Dec. 14, 1905	30,000	2.000	2	6.0	200
Dec. 14, 1905	30.300	2.600	4	6.0	198
Dec. 15, 1905	30,900	2,100	2	5.5	178
Dec. 15, 1905	31.300	1.000	2	5.9	188
Dec. 15, 1905	30,000	1,300	5	5.8	193
Dec. 18, 1905	29,900	5,600	4	5.6	172
Dec. 18, 1905	31,000	1,000	5	5.6	181
Dec. 18, 1905	28,500	1.200	1	5.5	193
Dec. 19, 1905	30.000	750	2	5.5	183
Dec. 19, 1905	29,000	550	4	5.6	193
Dec. 19, 1905	27,000	9,900	19	5.6	208
Dec. 19. 1905	28.000	6,000	3	5.5	197
Dec. 19, 1905	30.000	3.700	4	5.5	183
Dec. 20, 1905	29.000	2.900	1	5.5	190
Dec. 20, 1905	28.400	4.100	2	5.6	197
Dec. 20. 1905	28,400	7,100	5	5.6	197
Dec. 20, 1905	28,000	5.900	5	5.8	207
Dec. 21. 1905	29,000	8,600	13	5.5	190
Dec. 21. 1905	28.000	8,700	11	5.5	197
Dec. 21, 1905	27,000	16,400	15	5.8	215
Dec. 21, 1905	26.000	2,700	6	5.5	212

Concerning this process of water purification, it may be said that it is the embodiment of simplicity. It is entirely mechanical and automatic. Electric switch is turned, two or three valves are opened, and the operation needs no further attendance. Electric current is taken from the city's wires to operate a motor generator, producing a current of 100 cycles, which is raised by transformers and condensers to a 10,000 voltage. By the operation of reactance coils and condensers, voltaic arcs and sparks are prevented, and the current passes as a pencil of blue light from each of some millions of metallic discharge-points across a short air gap to nickel receivers. Atmospheric-air is drawn across this gap by means of an air-pump, and in so passing is partially converted into ozone. The ozonized air is then forced through a stand-pipe, in which it meets a current of water flowing in the opposite direction. The contained bacteria are instantly destroyed by the ozone.

The reason of this is extremely simple. Chemical analysis of the bodies of bacteria show that they are made up of 84 per cent. of water, and about 16 per cent. of solids. Of these solids more than half is made up of carbon. The strong affinity of oxygen for carbon is well known. Ozone, being a concentrated form of oxygen, has an even greater affinity for carbon; and the moment a bacillus comes in contact with a bubble of ozonized air the carbon of its body combines with oxygen, and the bacillus is consumed as completely as if it had touched a flame. Indeed, the process is analagous to that of combustion. Just as though burnt up, nothing remains of the bodies of the bacteria but carbonic acid gas, which partially rises to the surface of the water and passes off into the air, and is partially taken up by the water. This gives it its brightness and pleasant taste.

So, too, with much of the soluble organic matter contained in the water, the invisible products of animal and vegetable decay. These are largely oxidized, and similarly rise as gas through the water. In this way discolered water is made bright and sparkling, and the putrescence resulting from decaying organic matter is removed with its causes.

On the other hand, nothing of a deleterious nature is added to the water. Compounds of copper, sulphur and other injurious chemicals have no place in ozonization. Ozone-purified water is simply H_2O, with a little more free oxygen than is usually found in natural waters.

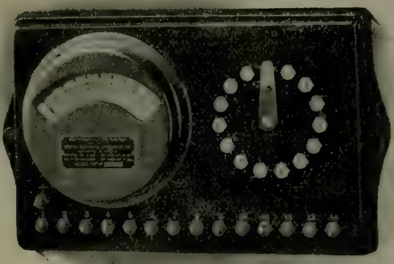
Naturally, the cost of any system of water purification is an important question where large public supplies are under consideration. The tests made in Philadelphia show that this is less than the usual methods of sand filtration. The ozone plant in West Philadelphia, large enough to give absolute purity to the water supply of a city of 30,000 inhabitants, has not cost more than the tithe of a sand filtration plant of equal capacity. Its operation also costs less. Moreover, it occupies a building only 30 by 50 feet, instead of covering many acres, as all sand filters do. Such a plant can be built in a few months; sand filtration takes years to instal.

With all these advantages, the ozonization process gives a perfect result. No disease-producing germs escape destruction in the ozonizing tower. In no other process has such a result been achieved.

To the foregoing advantages should be added that arising from the purely mechanical character of the process of ozonization. The elimination of disease germs from a city's water supply is not dependent upon the care and attention of dozens of unskilled laborers. It is not conditioned upon the thoroughness with which many acres of filtering areas are cleaned. It is not affected by the accuracy with which an Italian or a Slav workman may remove an inch or two of a mud deposit. None of the elements of human liability to err are involved in ozonization. A skilled mechanic moves a switch, turns a few valves, watches the meters for a few moments, and then the entire system runs automatically day and night with no further attention than the oiling of the bearings and the cleaning of the machinery. If need be, the doors of the building may be closed, and the machinery left to run itself. So far as mechanical perfection applied to hygienic ends can be reached, it is in the ozone treatment of public water supplies.

INDEX.

Weston Electrolytic Voltmeter



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